THESIS FOR THE DEGREE OF MASTER OF SCIENCE

RADIOCHEMICAL INVESTIGATION OF UNSATURATION IN POLYSTYRENE PREPARED BY CATIONIC MECHANISM

SYED. I. HAIDER, B.Sc. (Kar.)
PGHP. Tech. (Dipl.)
B.I.T. (Bfd.)

SUPERVISOR. DR. IAN. C. MCNEILL,
Macromolecular Chemistry Department,
GLASGOW UNIVERSITY.

JUNE, 1965.

CONTENTS.

PREFACE

The work described in this thesis was carried out in the period OCTOBER, 1962 to MARCH, 1965 at the UNIVERSITY OF GLASGOW in the department of physical chemistry, which is under the supervision of Prof. J. M. Robertson, F.R.S.

I gratefully acknowledge the assistance given me by the technical staff of this department in particular Messrs. R. Smith and R. G. Perrett for general technical assistance, Messrs. M. Riggans and F. Harvey for constructing many pieces of metal apparatus and Messrs. T. J. Pitt and J. Connolly for supplying various parts of glass apparatus associated with my vacuum line.

I am also particularly grateful to Messrs. J. C. Lawrence, T. M. Makhdumi, J. K. Pang, R. McGuchan, I. F. McLaren and Dr. I. Meldrum for initiating many stimulating discussions in various aspects of this work.

Finally I would like to thank Dr. Ian C. McNeill for his invaluable help and guidance during the course of this work and for giving me the opportunity to continue the work for an extra six months.

SUMMARY

RADIOCHEMICAL INVESTIGATION OF UNSATURATION IN POLYSTYRENE PREPARED BY CATIONIC MECHANISM

Unsaturation in 'cationic' polystyrene is of interest for two main reasons: because of its importance in providing some evidence about the polymerisation process, particularly the termination mechanism, and to help clarify the mechanism of degradation - particularly by providing information as to the presence of main chain unsaturation which might be associated with "weak links".

Styrene was polymerised 'cationically' at - 78°C using stannic chloride, $SnCl_4$, as catalyst and methylene chloride, CH_2Cl_2, as solvent. Five polymer samples were prepared and purified by precipitation from carbon tetrachloride using methanol as non-solvent. The number average molecular weights of the polymers were measured in benzene solution and all the five polymer samples were found to be of very much of the same molecular weight within experimental error. This was taken as evidence that the polymerisation conditions were reproducible. Polystyrene was fractionated by both gel-filtration, and precipitation techniques.

Polymer unsaturation was determined by reaction with (^{36}Cl) chlorine of known specific activity. Known quantities of radio-chlorine were distilled by the usual cold line vacuum technique

into solutions of polymer in carbon tetrachloride. The reaction was carried out in sealed tubes at 25°C in absence of air and light. The chlorinated polymers were purified to remove excess of chlorine by three precipitations from carbon tetrachloride solution using methanol as precipitant. Solutions of radiochlorinated polymers were counted in a liquid counter.

These chlorination experiments indicated that there was one double bond per polymer chain. A plot of unsaturation against the inverse of the number average molecular weight gave a straight line passing through the origin, indicating that the unsaturation was exclusively terminal. This supports the proton expulsion theory of chain termination in "cationic" or "pseudocationic" systems, and suggests that under the conditions in which these polymers were prepared, other chain termination processes are of negligible importance.

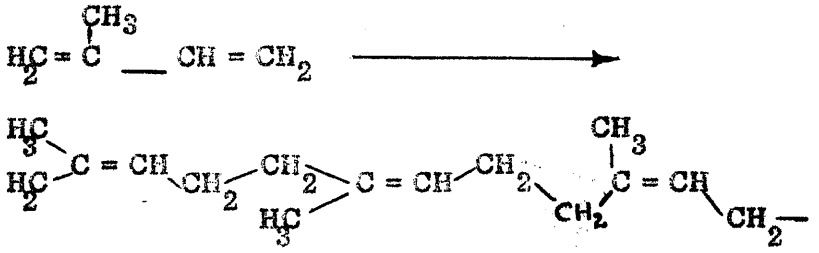
A fractionated sample of polystyrene, number average molecular weight $\bar{M}n$ 425,000, was degraded at 325°C under vacuum and the drop in molecular weight was plotted as a function of loss of weight. The initial steep fall was completed very early in the reaction. Thus despite the complete absence of main chain unsaturation, "cationic" polystyrene shows similar degradation properties to material prepared by a free radical mechanism. This important result leads to the conclusion that if polystyrene possesses any weak links, they cannot, as previously supposed,

be due to unsaturated structures.

On the other hand, the observed degradation behaviour is consistent with theories of a small amount of random scission or intermolecular transfer.

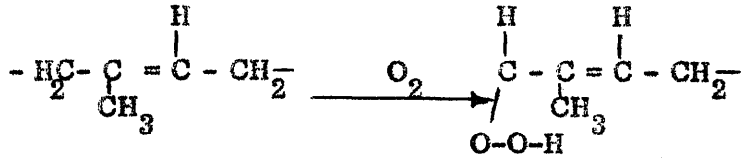
IMPORTANCE AND ORIGIN OF SMALL AMOUNTS OF UNSATURATION IN POLYMERS.

Small amounts of unsaturated centres in polymer chains are important for a number of reasons. They may form centres for cross linking reaction, as in vulcanization of rubbers, points at which modification of the polymer can be brought about by reaction such as grafting, points of weakness towards oxidative attack or centres at which degradation may be initiated. The isoprene units in rubber are linked head to tail in the cis configuration:



POLYISOPRENE - RUBBER.

Raw rubber is soft and tacky and the tensile strength and resistance to abrasion are low. The properties are changed markedly by vulcanization which consists in heating rubber with 5 - 8% of sulphur. The nature of the vulcanization process is uncertain, but it undoubtedly involves establishment of sulphur cross-links between hydrocarbon chains. Initial attack is probably not at double bonds of the polyisoprenoid chain, but at activated allylic positions. Similarly, allylic oxidation to a hydroperoxide is probably the first step in the ageing of rubber due to air oxidation. As a result of the oxidation process



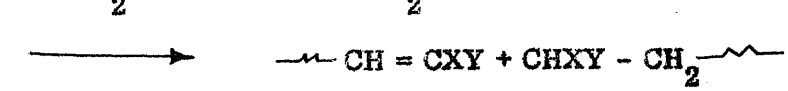
the long chains of atoms are broken, a comparatively small amount of oxidation doing considerable damage. If there are ten thousand units in the structure of the rubber molecule then the breaking of one link is sufficient to reduce the average molecular size to five thousand units. Ten links broken would bring the average chain length down to only one thousand units and yet it would be impossible chemically to detect such a small amount of oxidation. The effects of oxidation are better revealed by the much larger change in mechanical properties which it brings about.

Grassie and Melville[1,2] showed the importance of unsaturated ends in the degradation of polymethylmethacrylate, which degrades on heating by first being rendered unstable at the ends of polymer chains, this being followed by a chain degradation reaction which yields only monomer. Grassie and Melville concluded that the ends involved are the saturated and unsaturated ends resulting from disproportionation in the chain termination process. One of these ends, the unsaturated one, is much less stable than the other. The energies of activation of the degradation reaction through the two types of bonds were estimated to be 31 and 42 K cals. It is possible to vary the rate of initiation by changing the nature of the end groups in the polymer molecules. Once this initiation has

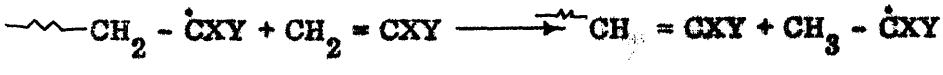
occurred there is no change in the characteristics of the depolymerization. More recently it has been shown[48] that the process with the higher energy of activation is due to initiation by random scission of the chain, and not as previously supposed.

In polyvinyl chloride, unsaturation could activate the chain for hydrogen chloride loss producing further unsaturation and leading eventually to the complete degradation of the chain to a conjugated polyene:

both in the main chain of a polymer or at the chain ends. One instance of terminal unsaturation has been given (the case of polymethyl methacrylate) in which the double bonds arise by disproportionation of free radicals in the termination process of free radical polymerisation.



Another reaction in free radical polymerisation which results in terminal unsaturation is transfer to monomer,



Some of the mechanisms of termination for cationic polymerisation as discussed subsequently could lead to double bonds at the chain ends.

Except in the case of diene polymers, the unsaturations we have been discussing are very low, of the order of 0.01 to 0.1% for polymers of molecular weights of commercial value. For this reason their direct detection (e.g. by spectroscopy) is not possible and their estimation is extremely difficult. Nevertheless it is apparent that useful information could be obtained about polymerisation mechanisms if this were possible, and indications of their concentration could be of the utmost value in degradation studies.

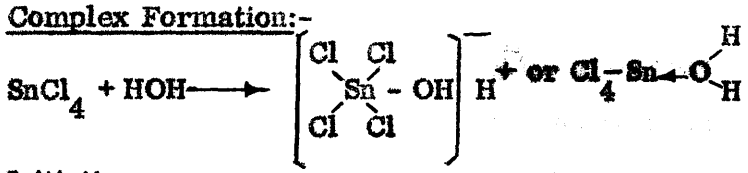
COMPARISON OF THE CATIONIC AND PSEUDOCATIONIC MECHANISMS OF POLYMERISATION.

Although this subject has been reviewed thoroughly it was considered to be useful to re-examine it in the light of some recent developments. Most important of these developments is the discovery that the polymerisation of styrene by perchloric and other acids and by stannic chloride and water is not an ionic process[3,4,5].

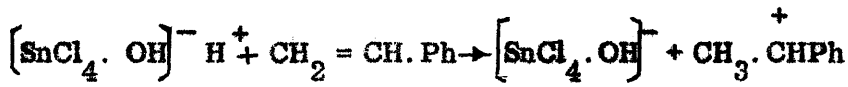
Plesch, Gandini[6] and other workers[7,8,9] have shown that probably almost all the polymerisations of styrene and some of the related monomers by conventional acids and by stannic chloride in hydrocarbons and chlorinated hydrocarbons are of pseudocationic type. An interesting aspect of pseudocationic polymerisations is that they are relatively insensitive to water which may be without effect on the kinetics even in concentrations up to ten times greater than that of catalyst. This is of great diagnostic value since the carbonium ions derived from polymerisable olefins are instantly destroyed by water if the inorganic catalyst is a conventional acid. If it is a metal halide, water may form a catalytic hydrate and its effect on rate and degree of polymerisation (D.P.) will depend on its concentration relative to the catalyst, and other factors.

A) CATIONIC MECHANISM (STYRENE)

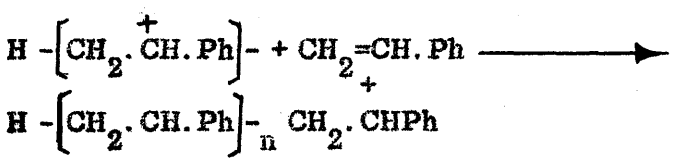
i) Complex Formation:-



ii) Initiation:-

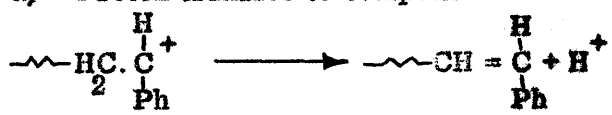


iii) Propegation:-



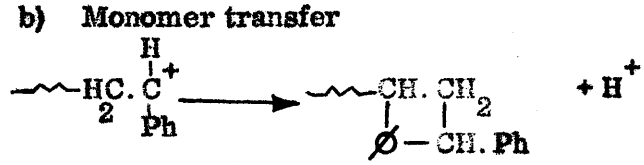
iv) Termination:-

a) Proton transfer to complex



unsaturated.

b) Monomer transfer



Indene type.

B) PSEUDOCATIONIC MECHANISM, (STYRENE).

i) Complex formation:- $SnCl_4 + HOH \longrightarrow SnCl_4.HOH$

ii) Initiation:- $CH_2 = CH.Ph + SnCl_4.HOH \rightarrow (OH.SnCl_4.CHPh.CH_3)$ Solv.

$(OH.SnCl_4.CHPh.CH_3)$ solv + C_8H_8 styrene

$(OH.SnCl_4.CHPh \leftarrow CH_2.CHPh \rightarrow_3 CH_3)_{Solv.}$

It is suggested that in the pseudocationic polymerisation, the propagating species is this complex between Lewis acid and monomer which has the composition $(HA.4\ C_8H_8)_{Solv.}$ and that it participates in the equilibrium.

iii) Propagation:-

$OH.SnCl_4.CHPh \leftarrow CH_2.CHPh \rightarrow_3 CH_3)^+_{Solv.}$ C_8H_8 styrene

$(OH.SnCl_4.CHPh \leftarrow CH_2.CHPh \rightarrow_n CH_3)$

iv) Termination:-

a) $\sim CH_2 - CHPh - CH_2 - CHPh - CH = CPhH$

unsaturated.

b) $\sim CH_2 - CHPh - CH_2 - CHPh - CH_2 - CH(\text{Ø} - CHPh) - CH_2$

Indene type.

The pseudocationic polymerisations are tentatively explained in terms of an ester as the active species. For the styrene/perchloric acid system it is known that this ester is only stable in the presence of an at least four fold excess of styrene. When, at the end of a polymerisation the styrene concentration has fallen to this level, the ester ionises. When styrene is mixed with an excess of acid in dilute solution, protonation is the only reaction.

The dead polymer formed in the above reactions may have either unsaturated or indene end groups, according to the temperature, catalyst and solvent. The indene end groups can either be formed directly or by the subsequent reaction of unsaturated end groups under the influence of the catalyst, as the cyclization is essentially a Friedel-Crafts alkylation.

It is clear from the above discussion that measurements of the very low unsaturations in polymers prepared by these mechanisms could give useful evidence of the relative importance of various chain termination processes. No main chain unsaturation would be expected. Studies of end structures in polymers prepared cationically have so far been confined to a very few cases using very low molecular weight material.

THERMAL DEGRADATION OF ORGANIC POLYMERS.

For the full understanding of the mechanism involved in the thermal degradation of organic polymers, it is necessary to know, among other factors, these three fundamental things:

i) The change of molecular weight of the polymer as a function of temperature and extent of degradation.

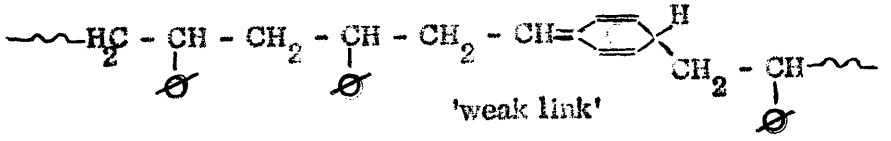
ii) The qualitative and quantitative composition of the volatile and non-volatile products of degradation.

iii) The rates and activation energies of the degradation processes.

With regard to the change of molecular weight with temperature and extent of degradation, a lot of work has been done in this department. The information which is available indicates that in most cases the molecular weight drops initially very rapidly during the first few per cent loss of weight. Beyond this the drop is slow.

The main features of the degradation of polystyrene in vacuo have been established by Jellinek[10], Madorsky[11], Grassie and Kerr[12] and Grassie and Cameron[13]. The rate of degradation reaches a maximum at about 35 - 40% degradation. There is an initial steep drop in molecular weight to values not far from 100,000. From about 15% conversion the drop in molecular weight becomes quite gradual.

All the above authors, except Madorsky[14], have accounted for the initial sharp fall in molecular weight in terms of a limited number of "weak links". Jellinek[15] supposed these to be oxygenated structures, but this was disproved by Grassie and Kerr who proposed the "quinonoid type" weak link structure, supposedly the result of an abnormal propagation through the benzene ring:



Support for the idea of weak links came from Grassie and Cameron's[13] solution degradation studies and from ozonolysis experiments which suggested that the polystyrene samples studied (prepared by free radical and anionic mechanisms) contained main chain double bonds at a concentration of the order of one per 1000 monomer units.[47]

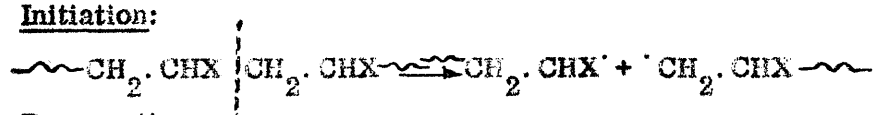
As to the nature of the products of degradation, systematic qualitative and quantitative analyses indicate that some polymers, for example, polytetrafluoroethylene and poly-α-methyl-styrene, yield on pyrolysis in a vacuum at temperatures up to about 500-600°C almost 100% monomer, while in the case of polyethylene pyrolysis under similar conditions yields a spectrum of hydrocarbon fragments varying in molecular weight from 16 (CH_4) to about 1000.

Intermediate between these two extremes are polymers that yield on pyrolysis a mixture of monomers and chain fragments of

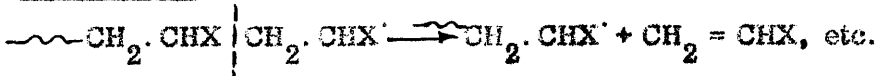
varying sizes. There are also polymers like poly(vinyl chloride) and poly(methylacrylate) which yield on pyrolysis fragments not related in structure to the polymer chains from which they derive, along with fragments that are parts of the chains.

Simha, Wall, Blatz and others[16,17,18,19] have proposed a mechanism for thermal degradation of polymers such as polystyrene and poly-α-methylstyrene in terms of a random scission process followed by inter or intra molecular transfer as follows:

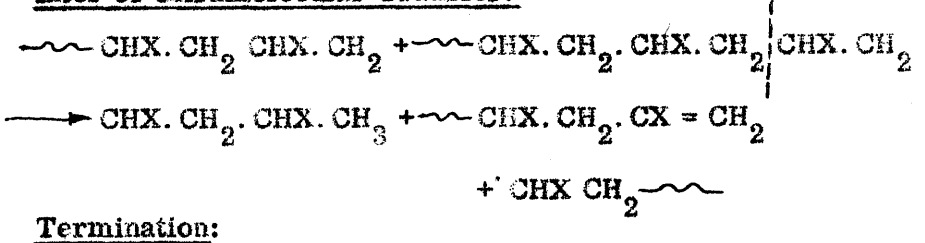
a) Initiation:



b) Propagation:



c) Inter or Intramolecular Transfer:



d) Termination:

2 free radicals ⟶ Polymer molecule.

They derived a theoretical expression for the rate of conversion of polymer to volatile material. The expression gives a rate maximum at 25% conversion. These authors explained the difference between the theoretical figure of 25% and the experimental one of 30 - 40% by postulating that the intra molecular transfer and monomer producing reactions are more important than

the randomising intermolecular transfer.

More recently Gordon[20,21] has re-examined the results of previous authors and has claimed from a theoretical stand point, that there is no need to invoke a "weak link" theory to explain the degradation of polystyrene. The scheme which Gordon supports is similar to that proposed by Simha, Wall and workers. Simha and Wall's mechanism for the initial production of free radicals does not preclude a "weak link" break down but any change in molecular weight produced by this initial step would be obscured by the resulting randomising effect of intermolecular transfer.

It is clear that studies of the degradation behaviour, and estimation of double bond concentrations in polystyrene prepared cationically should help to resolve the conflict between the two degradation theories.

MEASUREMENT OF UNSATURATION IN POLYMERS.

Comparatively few methods for unsaturation determination in small molecules have been successfully applied to polymers. With one exception, those that are available can only be used down to unsaturations of about 0.5 mole per cent.

Iodine - Mercuric Acetate Method: This is a standard procedure used for determination of unsaturation in butyl rubbers and has been described by Gallo, Weise and Nelson[22]. A solution of butyl rubber in carbon tetrachloride is reacted for 30 minutes with iodine in the presence of mercuric acetate and tri-chloroacetic acid. The excess iodine is titrated with sodium thiosulphate. The iodine number (centigrams of iodine per gram of polymer) is calculated from:

$$\text{Iodine number} = \frac{\text{ml x N of } Na_2S_2O_3 \text{ x } 126.91 \text{ x } 100}{\text{gms. of sample x } 1000}$$

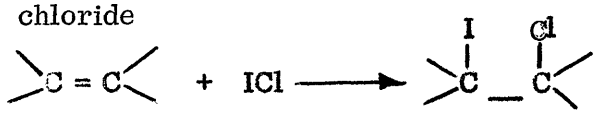
The mole per cent unsaturation is related to the iodine number by:

$$\text{Mole per cent unsaturation} = \frac{M \text{ (Iodine number)}}{126.91\ F}$$

where M is average molecular weight of monomer unit and F is a stoichiometric factor depending on reaction conditions.

The addition of halogens to a double bond is often a reliable method for determination of unsaturation. In butyl rubbers, however, there are complicating reactions and the reliability of results from halogen procedures has been subject to question.

Iodine Chloride Method: This was put forward by Lee, Kolthoff and Johnson[23]. It is based on the addition of iodine chloride to a carbon-carbon double bond. The precedure consists in adding excess iodine chloride



to a solution of an unsaturated compound and after a suitable reaction period determining by titration the amount of iodine chloride remaining. This iodine chloride method yields accurate results for most olefins and polymers. However, when iodine chloride is added to highly branched olefins and polymers, the reaction is abnormal in that the addition products formed possess steric strain and tend to decompose. The decomposition products react further with iodine chloride, thus leading to high unsaturation values. Modified calculations of unsaturation from iodine chloride results give values which are considered reliable for butyl rubbers. The results so obtained give good agreement with values obtained by the iodine - mercuric acetate method.

McNall and Eby's[24] Method: They prepared samples of butyl rubbers with known unsaturations by using C^{14}-labelled isoprene. They estimated the unsaturations by using the Iodine - Mercuric Acetate method, which they found to be reproducible, but they had to increase the results by 15% to estimate accurately the amount of isoprene in the co-polymer. The iodine equivalent for this

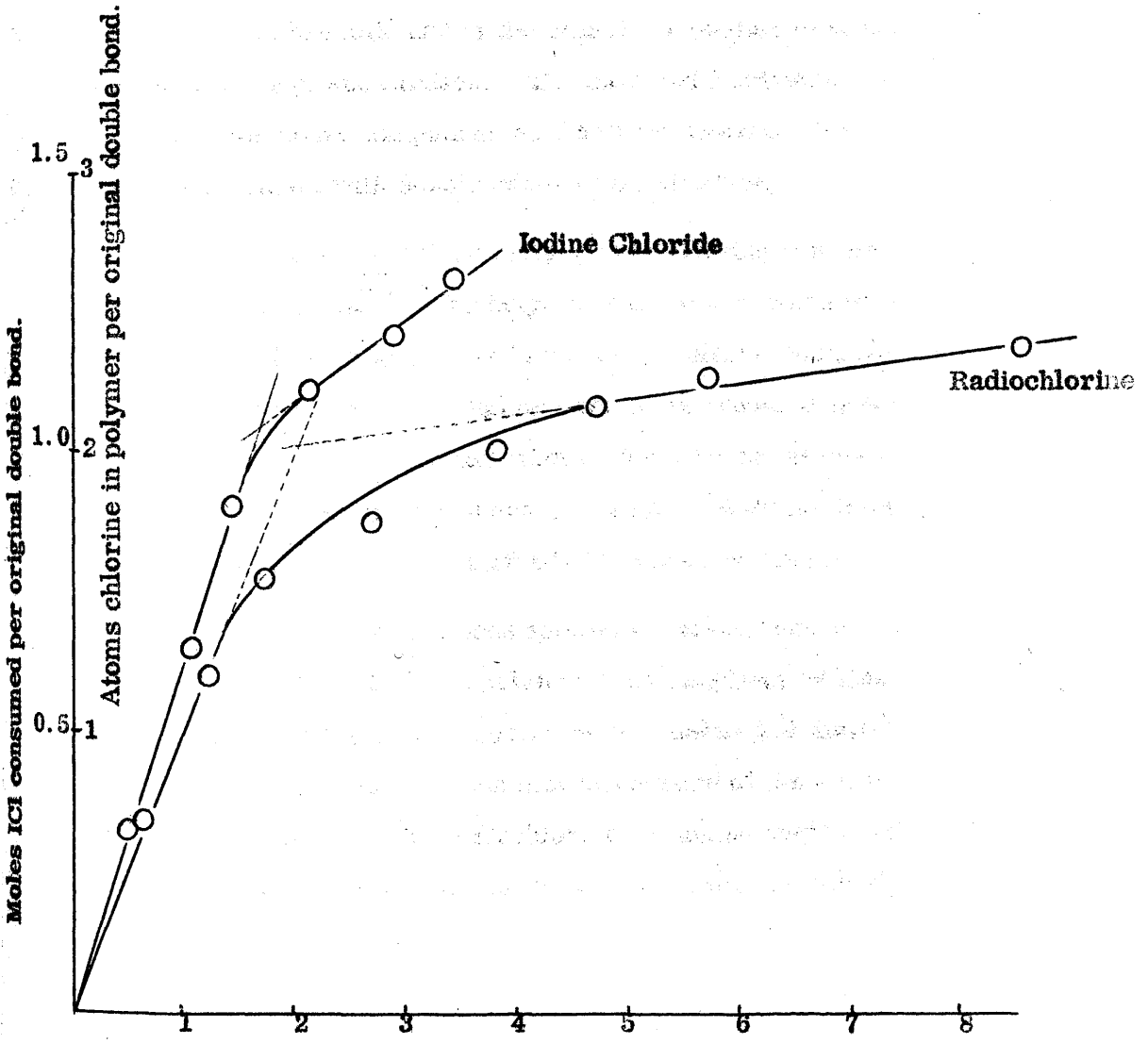
method is thus 2.61 instead of 3. The amount of diolefin entering the polymer was measured directly by isotope tracer techniques. This should determine the unsaturation accurately, assuming that there is one double bond for each molecule of isoprene entering the polymer. This assumption should be sound, because there is no evidence of cross-linking in the soluble butyl polymers and end group unsaturation is negligible. Dimers of isoprene in butyl rubber which could cause abnormalities in unsaturation measurements are also absent.

Kaufmann's Method:[25] This method, modified by Byrne and Johnson[26], can be used to measure polymer unsaturation. The polymer sample is allowed to react with an aqueous methanol solution of bromine and sodium bromide containing a little hydrochloric acid as a catalyst. The excess bromine is treated with potassium iodide solution and the liberated iodine treated with sodium theosulphate. This method has been tested with a number of pure compounds and it has been established that the halogenation of double bonds takes place without any substitution reactions. Sodium bromide is believed to form a complex which is a mild brominating agent with little tendency to substitute.

$$Br_2 + Na\,Br \rightleftharpoons Na\,Br.\,Br_2$$

$$R - CH = CH - R + NaBr.\,Br_2 \longrightarrow$$

$$R.CH.Br.CH.Br.R + Na\,Br$$



Moles halogen per mole original double bond in reaction mixture.

Figure 1 - Comparison of the reaction of butyl rubber with radiochlorine and with iodine chloride obtained by McNeill[27].

The solubility of sodium bromide in methanol is insufficient to provide the excess bromine ions necessary to complete bromination. Without excess bromide use of the reagent is subject to serious errors because of substitution. The modified Kaufmann's method is suitable for some compounds but has been found to give anamalous results with double bonds of acrylic type.

A radiochemical method using (^{36}Cl) chlorine has been used successfully by McNeill[27,28] for butyl rubbers with unsaturations around one mole per cent. As in the Lee, Kolthoff and Johnson method, a graph is drawn of halogen which has reacted versus halogen present in the reaction mixture for a series of mixtures. This is shown in Figure (1) where the reaction plots for the radiochlorine and iodine chloride methods have been compared.

This method has also been applied to polystyrene by Makhdumi and McNeill[29]; to poly(ethyl methacylate) by Mounter and McNeill[30] and to polyisobutene by McGuchan and McNeill[31]. In most cases the unsaturations measured were of the order of 0.01 to 0.1 mole %. The radiochlorine technique ought therefore to be ideally suited to a study of trace unsaturation in polystyrene.

PURPOSE OF THIS WORK.

By measuring the very low unsaturations of samples of polystyrene prepared using stannic chloride as catalyst at - 78°C, it was hoped to obtain useful evidence regarding,

a) The mechanism of chain termination in the polymerisation reaction. As had already been discussed, if proton expulsion is the chain terminating reaction each polymer molecule should possess one terminal double bond.

b) The mechanism of degradation of polystyrene. The weak link theory developed by Grassie and Kerr and Grassie and Cameron proposes that the polymer chain contains some unsaturated structures which behave as weak links.[12,13]

For the latter purpose, some degradation experiments on 'cationic' polystyrene were also necessary, to establish the nature of the molecular weight change in the course of the degradation, for comparison with data already available for polystyrenes prepared by free radical and anionic mechanisms.

PART II

EXPERIMENTAL TECHNIQUES.

THE PREPARATION OF CATIONIC POLYSTYRENE.

A) Purification of Materials:

Monomer: The inhibitor was removed from styrene by washing with caustic soda. The monomer was then washed with distilled water and distilled under reduced pressure. The middle fraction was collected. It was dried over pure calcium chloride and stored at 0°C. Monomer showed no signs of inhibitor or other impurities when tested by V.P.C.

Catalyst: The catalyst stannic chloride was supplied in tightly sealed screw capped bottles by B.D.H. Ltd., and used without further purification. It was also available in sealed glass ampoules.

Solvent: Methylene chloride was distilled at atmospheric pressure, the middle fraction being collected at $40.5^{\circ} \pm 0.05$, and stored in a Winchester bottle over dry calcium chloride.

Precipitant: Methanol used to precipitate the polymers formed after polymerisation was 'ANALAR'. The methanol used to precipitate polymers after reaction with radiochlorine was as supplied in bulk by I.C.I.

B) Preparation of Polymers:

The cationic polymerisation of styrene is comparatively free from many of the complicating side reactions which characterise the

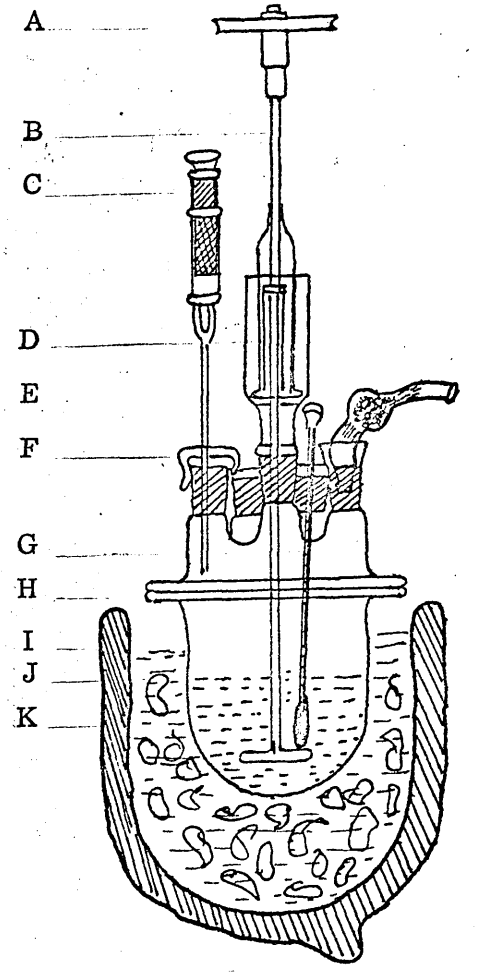


Figure 2 - Apparatus for cationic polymerisation of styrene.

A - Motor for the stirrer.
B - Polythene coated stirrer.
C - Hypodermic syringe.
D - Drying calcium chloride tube.
E - Rubber cap.
F - Alcohol thermometer.
G - Flanged reaction flask.
H - Vacuum flask.
I - Cooling mixture of dry CO_2 and methylated spirit.
J - Stirring gland.
K - Monomer - solvent mixture.

ionic polymerisation of other olefins. Polymers up to a molecular weight of approx. 40,000 can be obtained at room temperature by suitable choice of both catalyst and solvent.

Greatest interest, however, is centred on the high molecular weight polymers obtained at lower temperatures, when side reactions which limit the molecular weight are negligible. Suitable polymers were prepared in the present work at - 78°C. It was therefore considered desirable to obtain polymers whose molecular weight were not less than 100,000.

All parts of the apparatus were washed with chromic acid and "pyroneg" solution and dried at 100°C in an oven for about 30 minutes prior to assembly.

The reaction was carried out in a 700 mls round bottom pyrex glass vessel with a flanged lid having five necks (Figure 2). The reaction flask was equipped with stirring gland and stirrer, thermometer and a calcium chloride guard tube to protect it from the moisture. One of the two remaining parts was closed with a thin rubber cap. Through the fifth neck monomer was introduced at the time of polymerisation.

The reaction flask was partially immersed in a freezing mixture of solid carbon dioxide and crude methylated spirit at a temperature of - 78°C. 500 mls of solvent and 50 mls of monomer were cooled in the flask to - 78°C. At this stage 0.5 ml of catalyst

was added by a hypodermic syringe through the rubber cap into the solvent/monomer mixture which was kept constantly stirred throughout the course of the reaction. There was slight increase in the reaction temperature just after the addition of catalyst (increase being 1-2^{o}C). This was an indication of polymerisation. The reaction was continued until the temperature returned to its initial value.

C. Purification of Polymers:

The polymer-monomer mixture on removal from the reaction vessel was poured directly into methanol (about a litre) from which precipitated polymer was removed by filtration. The polymer was dried and dissolved in the minimum amount of carbon tetrachloride required. It was precipitated in excess of methanol (1-2 litres) by adding the solution drop by drop. A magnetic stirrer was used during each process of precipitation. The process was repeated twice to ensure the removal of residual monomer and catalyst. The precipitated polymer was allowed to dry overnight at room temperature and then it was left for at least fortyeight hours under vacuum to remove volatiles.

In all the polymerisations 50 ml of purified and dried monomer was used, and in each case the percentage yield of polymer obtained was 40% i.e. about twenty gms. All the five polymers were prepared under experimental conditions which were kept as nearly identical as possible.

MOLECULAR WEIGHT DETERMINATION.

Classical methods of molecular weight determination such as depression of freezing point and elevation of boiling point are applicable only to very low molecular weights, below about 10,000. There are two methods of measuring molecular weights which are commonly used in the range 100,000 to 500,000: viscometry and osmometry. However, only osmotic pressure measurements lead directly to the number average molecular weight which is required to calculate the number of double bonds per polymer chain from unsaturation determinations. Viscosity measurements lead to a molecular weight average which depends not only on the number of polymer molecules, but also on their size.

Molecular weights of the unfractionated polymers were determined in benzene solution using an osmometer of the type described by McNeill[32]. The trend in osmometer design has been towards large membrane areas and small capillaries. It is suggested by McNeill that this results in serious deficiencies and that a more satisfactory design is one in which the membrane area is very small and the pressure measuring tubes are wide. Such an instrument approaches osmotic equilibrium so slowly that over short period of times the observed head is almost constant, and thus the net rate of transfer of solvent across the membrane is constant. In this osmometer the osmotic pressures of polymer solutions are calculated from measurements of the rate of solvent diffusion at a

constant hydrostatic pressure. The results compared favourably with the results of the same polymers obtained using the Mechrolab High Speed Membrane Osmometer[33], now in use in this Department. Molecular weights of polymer fractions and degraded samples were measured using the latter instrument.

The number average molecular weight of a polymer (M_2) is related to the equilibrium osmotic pressure by the following equations:

$$\pi/C = \frac{RT}{M_2} + \frac{RT.d_1}{M_1 d_2^2}\left(\tfrac{1}{2} - \chi\right) C + \frac{RT\,d_1}{3 M_1 d_2^3} C^2$$

C = concentration in gms of solute per millitre of solution.

d_1 = density of solvent.

T = absolute temperature.

R = gas constant = 82.06 CC atmosphere per degree per mole.

d_2 = density of solute.

M_1 = molecular weight of solvent.

Since measurements were confined to solutions less than 1.5 gm/100 gm in concentration the third term could be neglected. Since

1 atmosphere = 1033.3 gm per Cm^2

π in atmosphere = hd/1033.3

where h is in centimeters and d is the density of the solution, and since

C in gm./ml = $C^1 d/100$

where C^1 is measured in g/100g

$$\pi/C \rightarrow_0 = \frac{L \times d}{1033.3} \times \frac{100}{d} = \frac{L}{10.33}$$

where L is the intercept or limiting osmotic head

$$\therefore \quad M_2 = \frac{10.33\ RT}{L}$$

$$M_2 = \frac{252,800}{L} \quad \text{at } 25^{\circ}C.$$

Osmotic pressure data for the five unfractionated polymers are given in figure 3. The molecular weights obtained are given in Table 1. The close similarity of all results is taken as evidence of reproducibility in the polymerisation conditions.

The molecular weights of fractionated polystyrene samples were obtained by the Mechrolab High Speed Membrane Osmometer,[33] Model 501, using toluene as solvent. Polymers II and IV were used, and the molecular weights of the fractions are given in Table 2.

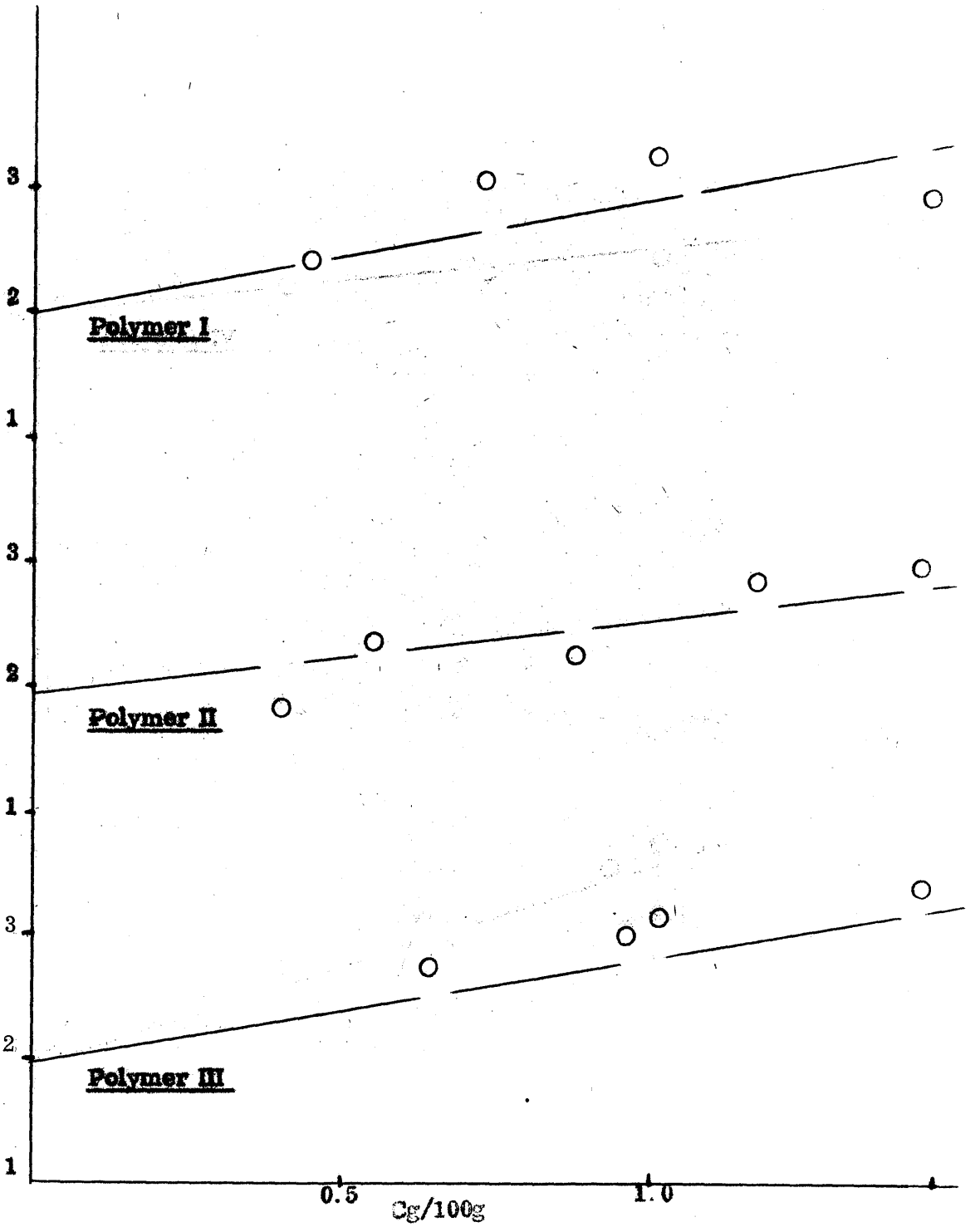


Figure 3 - Osmotic pressure data for unfractionated polymers.

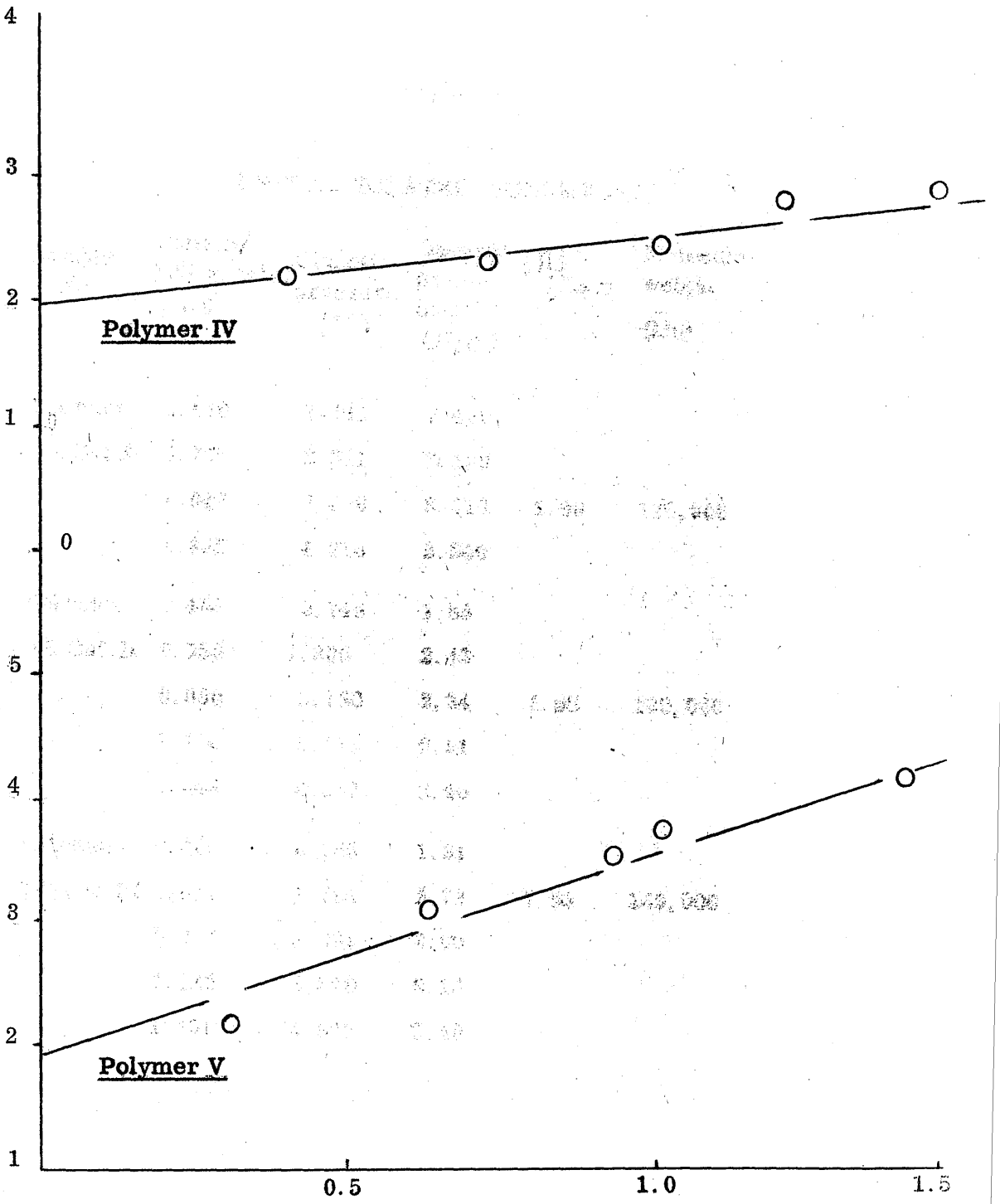


Figure 3 - (continued).

TABLE 1.

OSMOTIC PRESSURE DATA FOR UNFRACTIONATED POLYMERS.

Sample No.	Conc. g/ 100. g. soln. (C)	Osmotic pressure (π)	Osmotic press/ conc. (π/c)	$(\pi/c)_{c \to 0}$	Molecular weight ($\bar{M}_n$)
Polymer	0.450	1.111	2.460		
PS. Cat. I	0.737	2.311	3.130		
	1.047	3.470	3.310	2.00	126,000
	1.465	4.316	2.940		
Polymer	0.404	0.748	1.85		
PS. Cat. II	0.550	1.336	2.43		
	0.880	2.160	2.34	1.95	130,000
	1.170	3.411	2.91		
	1.443	4.338	3.00		
Polymer	0.409	0.785	1.91		
PS. Cat. III	0.644	1.794	2.78	1.95	130,000
	0.967	2.908	3.00		
	1.120	3.570	3.18		
	1.450	4.930	3.40		

TABLE 1 (contd.)

OSMOTIC PRESSURE DATA FOR UNFRACTIONATED POLYMERS.

Sample No.	Conc. g/ 100 g. soln. (C)	Osmotic pressure (π)	Osmotic press/ conc. (π/c)	(π/c) $c \to 0$	Molecular weight ($\bar{M}n$)
Polymer	0.405	0.904	2.23		
PS. Cat. IV	0.725	1.650	2.28		
	1.033	2.492	2.41	1.95	130,000
	1.205	3.384	2.81		
	1.446	4.144	2.86		
Polymer	0.309	0.926	2.32		
PS. Cat. V	0.631	1.959	3.10		
	0.927	3.290	3.54	1.92	133,000
	1.078	4.010	3.71		
	1.396	5.717	4.09		

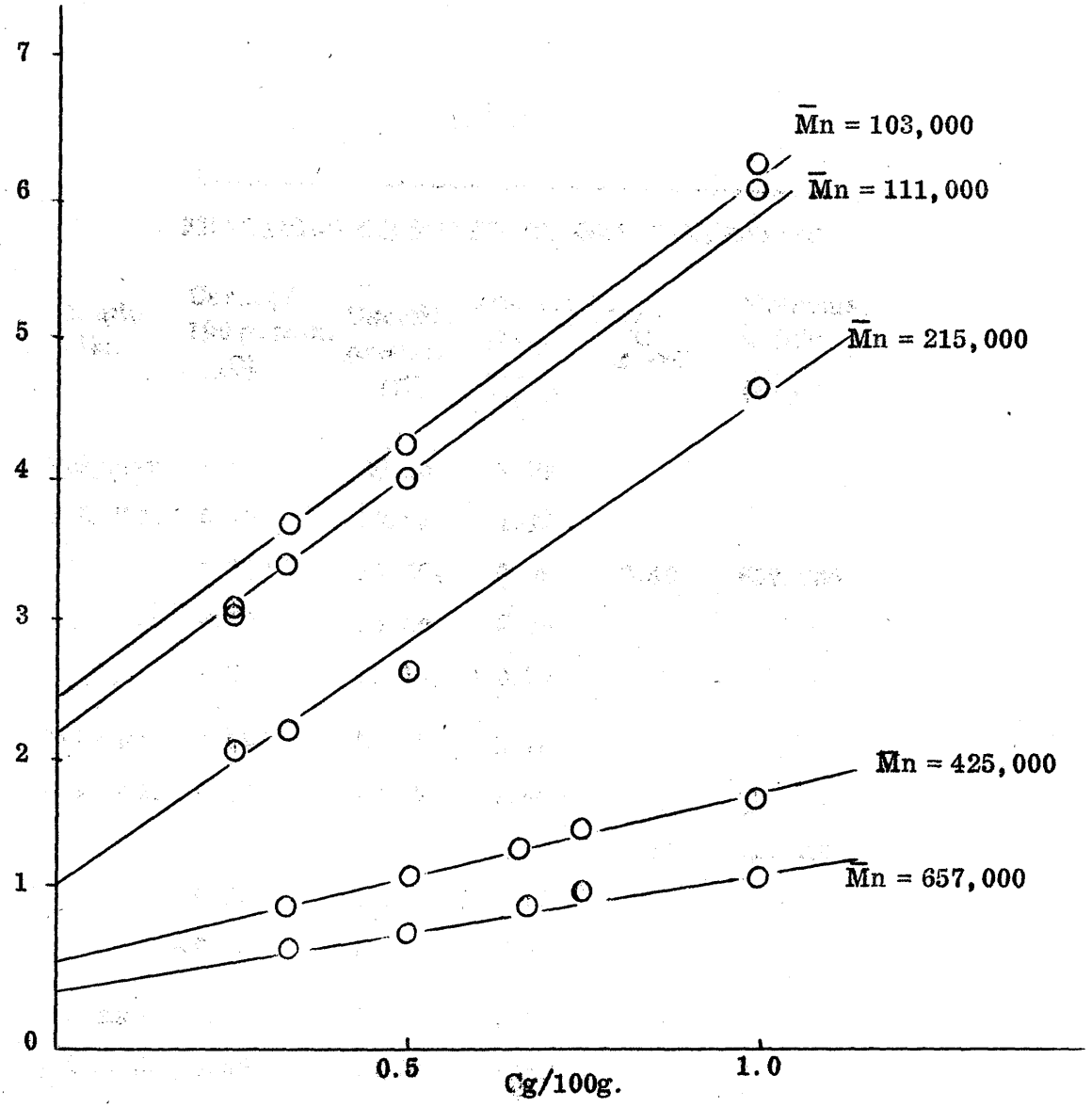


Figure 4A - Osmotic pressure data for polymer fractions obtained by Gel - Filtration.

TABLE 2

OSMOTIC PRESSURE DATA FOR POLYMER FRACTIONS OBTAINED BY GEL FILTRATION.

Sample No.	Conc. g/ 100 g. soln. (C)	Osmotic pressure (π)	Osmotic press/ conc. (π/C)	$(\pi/C)_{C \to 0}$	Molecular weight $\bar{M}_n$
Polymer	1.00	20.10	1.20		
P II. F 1.	0.75	19.74	1.12		
	0.67	19.56	0.99	0.40	657,000
	0.50	19.30	0.80		
	0.33	19.13	0.70		
Polymer	1.00	20.58	1.78		
P II. F 2.	0.75	19.97	1.56		
	0.66	19.73	1.40	0.62	425,000
	0.50	19.40	1.20		
	0.33	19.14	1.02		
Polymer	1.00	23.32	4.68		
P II. F 3.	0.50	19.96	2.64		
	0.33	19.38	2.24	1.15	215,000
	0.25	19.17	2.12		

TABLE 2 (contd.)

OSMOTIC PRESSURE DATA FOR POLYMER FRACTIONS OBTAINED BY GEL FILTRATION.

Sample No.	Conc. g/ 100 g. soln. (C)	Osmotic pressure (Π)	Osmotic press/ conc. (Π/C)	$(\Pi/C)_{c \to 0}$	Molecular weight ($\bar{M}n$)
Pblymer	1.00	25.62	6.07		
P II. F.4.	0.500	20.54	3.98		
	0.33	19.68	3.39	2.22	111,000
	0.25	19.33	3.11		
	1.00	24.56	6.26		
Polymer	0.50	20.42	4.23		
P II. F.5.	0.33	19.53	3.70	2.40	103,000
	0.25	19.16	3.04		

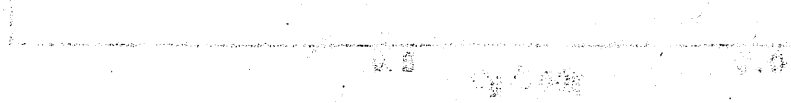


Figure 4.7 - Osmotic pressure data for polymer fract by fractional precipitation

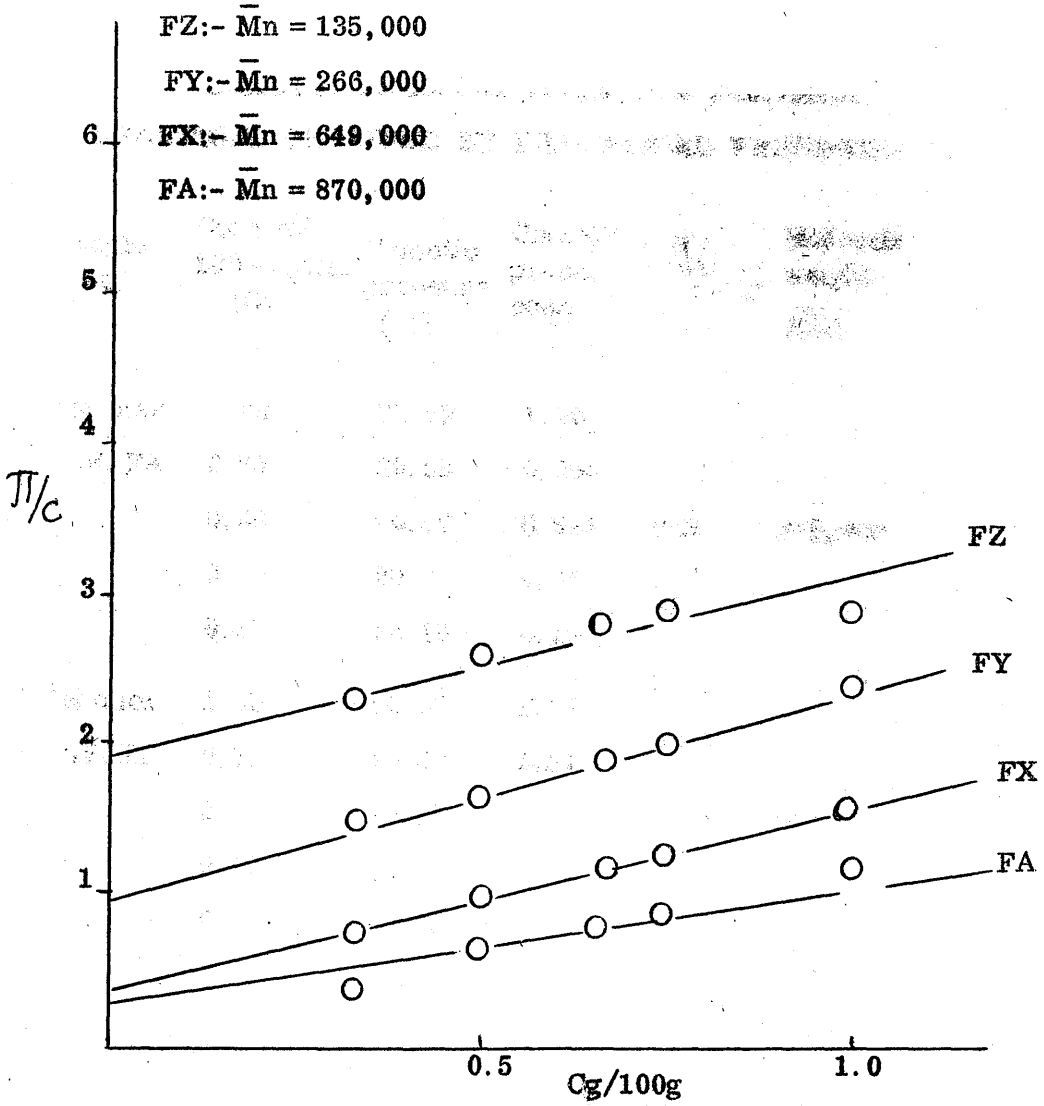


Figure 4 B - Osmotic pressure data for polymer fractions obtained by Fractional Precipitation.

TABLE 3.

OSMOTIC PRESSURE DATA FOR POLYMER FRACTIONS OBTAINED BY FRACTIONAL PRECIPITATION.

Sample No.	Conc. g/ 100 g. soln. (C)	Osmotic pressure (π)	Osmotic press/ conc. (π/C)	$(\pi/C)_{C \to 0}$	Molecular weight ($\bar{M}n$)
Polymer	1.00	21.22	1.20		
P IV. FA	0.75	20.69	0.894		
	0.66	20.57	0.825	0.3	870,000
	0.50	20.35	0.66		
	0.33	20.16	0.42		
Polymer	1.00	20.23	1.62		
P IV. FX.	0.75	19.59	1.31		
	0.67	19.43	1.22	0.38	640,000
	0.50	19.11	1.00		
	0.33	18.85	0.73		

TABLE 3 (contd.)

OSMOTIC PRESSURE DATA FOR POLYMER FRACTIONS OBTAINED BY FRACTIONAL PRECIPITATION.

Sample No.	Conc. g/ 100 g. soln. (C)	Osmotic pressure (π)	Osmotic press/ conc. (π/C)	(π/C) $C \to 0$	Molecular weight ($\bar{M}n$)
Polymer	1.00	21.22	2.10		
P IV. FY.	0.75	20.34	1.63		
	0.67	20.11	1.48	0.99	266,000
	0.50	19.66	1.08		
	0.33	19.32	0.61		
Polymer	1.00	22.94	2.91		
P IV. FZ.	0.75	22.21	2.90		
	0.66	21.91	2.82	1.94	135,000
	0.50	21.32	2.58		
	0.33	20.80	2.31		

FRACTIONATION OF POLYSTYRENE.

Fractionation of polystyrene was carried out by two different methods,

(a) gel filtration. (b) fractional precipitation.

a) Gel Filtration: [34] The mechanism of gel filtration is not clear. It is assumed that the solute molecules penetrate the gel particles and the retardation of the molecules is differential in its nature so that the mechanism appears to be a type of molecular sieving.

When a solution of molecules of different size is run through the column, smaller molecules are retarded first so that the fractions obtained initially have higher molecular weights than that of the original mixture while the last fractions have lower molecular weights.

The air below the sintered glass was expelled (Figure 5) and replaced by solvent - this was to prevent channelling in the gel due to entry of air during column preparation. Santocel 'A' (Monsanto Chemical Co. Ltd.) was added as a slurry in portions of about 9 inches at a time and between additions the column was gently agitated with a length of wire, spiralled at the end, to remove all air bubbles which had entered with the gel. When the column had been filled it was eluted with solvent, toluene, overnight to allow the gel to pack down. Further gel had to be added to give the column height of 56 inches.

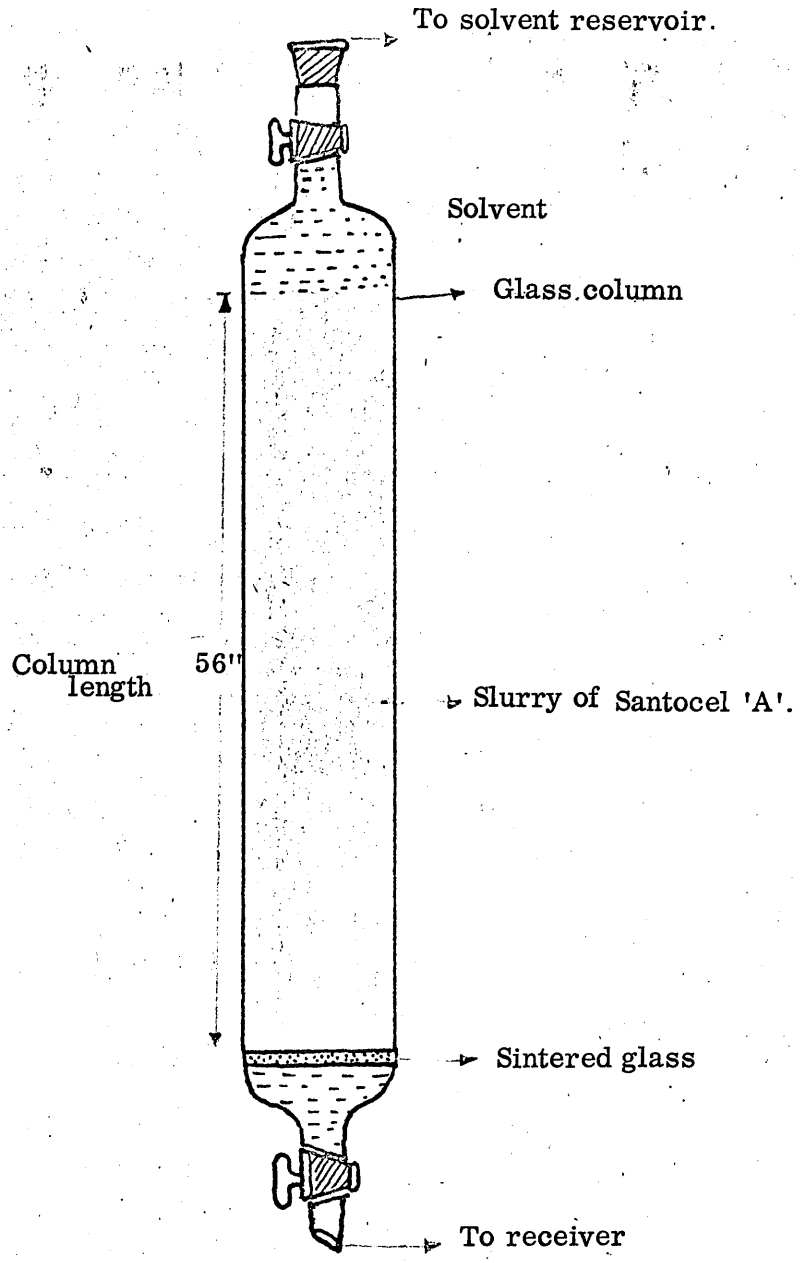


Figure 5 - Apparatus for gel-filtration.

In these experiments a sample of hetero-disperse polystyrene with number average molecular weight $\bar{M}_n$ = 130,000 was loaded on to the top of column and was eluted with toluene. 0.5 to 1 gram of polymer in 25 mls of solvent was added to the column and when this had run into the gel, the reservoir of the solvent was attached to the column and was eluted at a rate of 15 mls/hr[34]. With this column length the first fraction was obtained in about 16 hrs and the final fraction about 22 hrs later. The polymer fractions were recovered by direct precipitation into the non-solvent methanol. The fractions were freeze-dried and characterized by osmometery to determine the number average molecular weights.

b) Fractional Precipitation: Gel filtration is a time consuming process since very dilute polymer solutions must be used. It required considerable time for enough polymer to be obtained for chlorination experiments. It was, therefore, thought desirable to carry out fractional precipitation to provide enough fractionated polystyrene samples in a relatively short time.

The technique for the fractional precipitation[35,36] of polystyrene was as follows. A dilute solution (not over one per cent) of the polymer in methyethyl ketone was prepared. About 8 gms of polystyrene were dissolved in 1600 mls of methylethyl ketone (0.50%) because the more dilute the original solution the better is the fractionation, although the amount of solvent required becomes extremely large. While this solution was maintained at a constant

temperature, methanol was added until the solution became cloudy. This indicated that the highest molecular weight material present in the sample had precipitated from solution but was still suspended. The solution was then allowed to cool slowly to its original temperature which caused a fraction to precipitate out of the solution under almost equilibrium conditions. As this suspension stood, the precipitate slowly settled to the bottom of the flask as a gelatinous layer from which the supernatant liquor was decanted.

The entire procedure was now repeated on the main solution. That is to say more methanol was added to cause cloudiness. The solution was heated, cooled, decanted and the precipitate redissolved. This procedure was continued until most of the polymer had been precipitated. The number of fractions obtained was 4 - 5 and each fractionated sample weighed about 1.5 gms. The number average molecular weights were obtained by osmometry as already described.

PREPARATION OF RADIOCHLORINE.

The method described by McNeill[27] was used. 100-150 mgs of palladous chloride were weighed into a specially constructed two-necked flask (Figure 6). 5 - 10 ml of radioactive hydrochloric acid were then pipetted into the flask. The sides of the flask were washed down with distilled water and one neck was sealed by drawing it off. The flask was warmed gently in the flame of a micro bunsen to dissolve the palladous chloride and then to distil off excess hydrochloric acid. This pure hydrochloric acid of reduced specific activity was collected and put aside. When the palladous chloride was dry (care must be taken to avoid overheating in the final stages of the distillation) a plug of glass wool was inserted in the open neck of the flask, which was then connected to the receiving vessel on the vacuum system (Figure 7). The glass wool prevented spurting over of particles of elemental palladium or palladous chloride during the subsequent decomposition. The system was evacuated and pumped for several hours to remove the last traces of moisture from the palladous chloride. The receiving vessel was then cooled in liquid air. After isolation of the system, the bulb was heated with a luminous gas flame until a "palladium mirror" formed and all traces of the red palladous chloride had disappeared. After completion of the reaction the bulb was removed and the chlorine was distilled into the chlorine reservoir which was then closed by means of a stopcock.

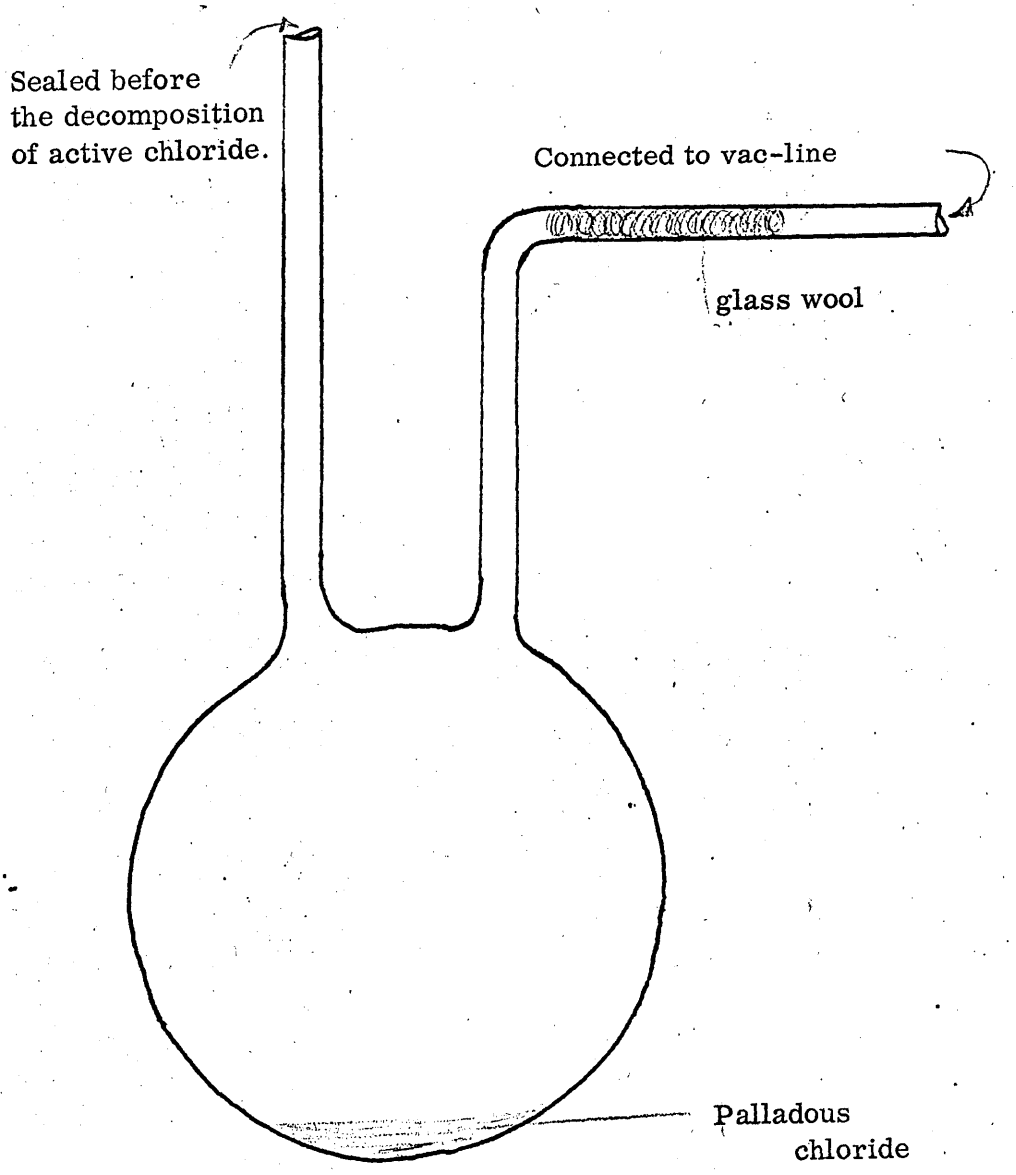


Figure 6 - Pyrex glass bulb for the decomposition of palladous chloride.

CALIBRATION OF RADIOCHLORINE GAS APPARATUS.

The apparatus for quantitative handling of radiochlorine is shown in Figure 7. Stopcocks A - D are the greaseless type supplied by G. Springham & Co. Ltd. By equilibrating the chlorine between the small and large bulbs and then closing stopcock A, a fixed fraction of the amount of chlorine orginally present in the reservoir may be removed. This process may be repeated as often as desired. The weight of chlorine delivered at each operation is related to that delivered the previous time by the relation;

$$\text{Wt. obtained} = \text{Previous weight} \times \frac{\text{volume of large bulb}}{\text{Total volume of both bulbs.}}$$

The ratio of volumes is determined as follows.

A reaction vessel was attached to the chlorine apparatus and 10 mls of decinormal potassium iodide solution was pipetted into it via the side arm which was then sealed off. The solution in the reaction vessel was frozen in the liquid air and degassed at least 3 - times by the usual technique. Stopcocks B, C and D were then closed and stopcock A was opened for about five minutes to equilibrate the chlorine between the small and large bulbs of the apparatus. Stopcock A was then closed, B opened and chlorine distilled into the reaction vessel. After five minutes the reaction vessel was sealed off, removed from the apparatus and placed in a thermostat at 25°C in a dark container for 5 minutes. Both arms of the reaction vessel were opened and the solution washed into a 50 ml conical flask. A

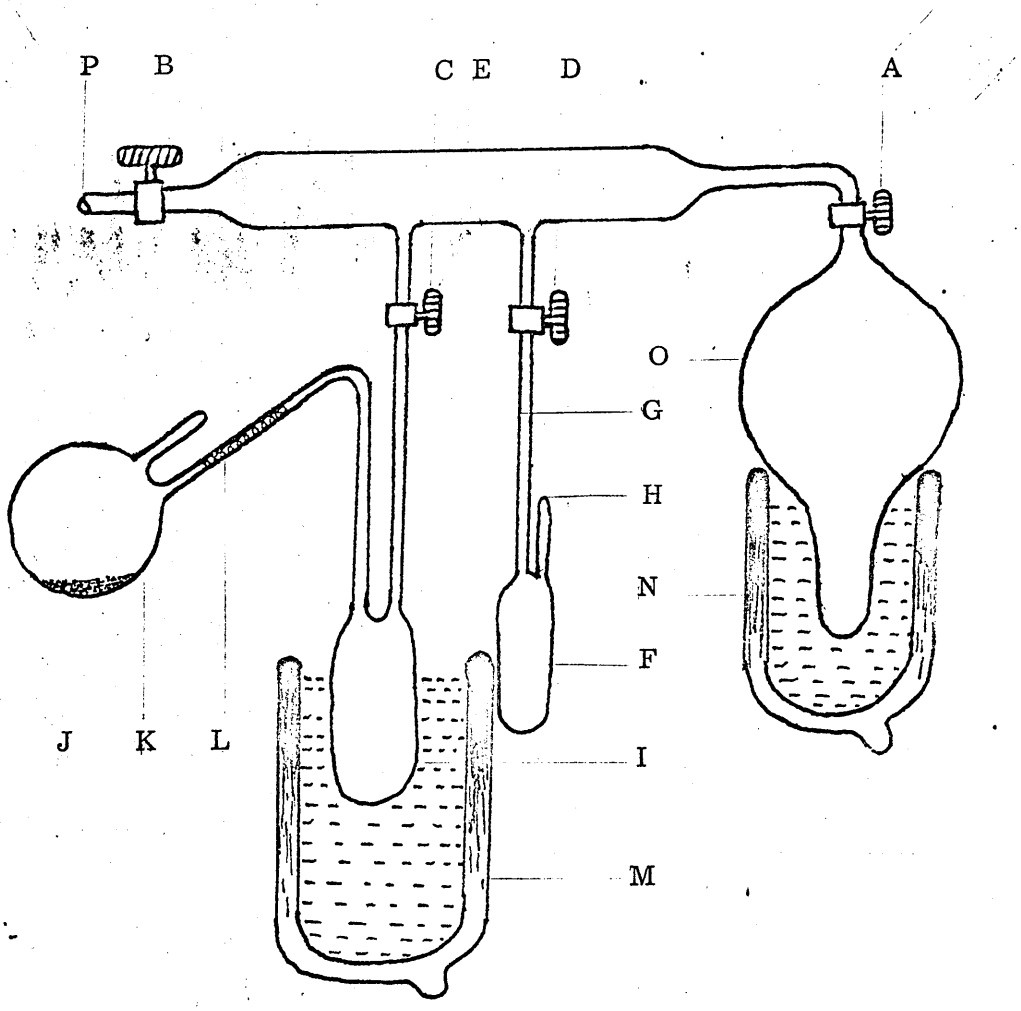


Figure 7 - Apparatus for handling radioactive chlorine.

A, B, C, D - Greaseless stopcocks.
E - Small bulb.
F - Reaction vessels.
G, H - Sealing points.
I - Chlorine collecting vessel.
J - Palladium Chloride.
K - Bulb containing palladium chloride.
L - Glass wool.
M, N - Vacuum flasks.
O - Large reservoir bulb.
P - Connection with the vac-line.

few drops of glacial acetic acid were added and the solution was titrated with N/10 sodium thiosulphate. Starch was used as indicator and was added when the solution was straw coloured. From this titration the amount of chlorine delivered by the gas apparatus was calculated.

$$\frac{\text{Amount of titre used} \times \text{Atomic Weight of Chlorine}}{10} = \text{mg of Chlorine distilled in the reaction vessel.}$$

The above procedure was repeated several times. Each aliquot of chlorine was absorbed in potassium iodide solution and titrated with sodium thiosulphate. The amounts of chlorine delivered by the apparatus were calculated and by working out the ratio of each amount of chlorine to the next the apparatus was calibrated. The ratio was found to be 1.160:1. (See Table 4).

The apparatus was also calibrated by a radio-chemical method. A reaction vessel was attached to the apparatus and 0.5 ml of styrene and 10 mls of carbon tetrachloride were added by means of a hypodermic syringe. The vessel was frozen in liquid nitrogen, evacuated to 10^{-4} m.m. and degassed three times. An aliquot of radiochlorine was distilled into the reaction vessel which was sealed off after five minutes and thawed out. After allowing one hour reaction time at 25°C the reaction vessel was opened and the contents poured into a 25 ml graduated flask. The reaction vessel was rinsed with cabbon tetrachloride and the solution was made up to the graduation

mark. 10 mls of the solution were pipetted into a liquid counter and counted over 30 minutes.

This procedure was repeated several times and the ratio of successive amounts of chlorine delivered by the apparatus was calculated by comparison of the counts obtained for each aliquot of chlorine. The final result obtained was in a very close agreement with that obtained using the previous method. (Table 4).

DETERMINATION OF SPECIFIC ACTIVITY OF RADIOCHLORINE.

A first aliquot of chlorine was collected in potassium iodide solution as above and the amount of chlorine delivered was found by titration with sodium thiosulphate. A second aliquot (containing a weight of chlorine which could be calculated from the previous weight and the calibration data for the apparatus, as already indicated) was absorbed in styrene/carbon tetrachloride solution as above and counted. Thus the activity due to a known weight of chlorine was calculated. The specific activity of the chlorine was expressed in terms of counts per minute per milligram of chlorine in carbon tetrachloride solution. In these experiments, the specific activities were in the range 1000 to 3000 counts/per minute per milligram of chlorine.

TABLE 4.

CALIBRATION OF RADIOCHLORINE GAS APPARATUS.

Operation No.	Thiosulphate titre.	Counts per minute.	Ratio.
1	2.915	-	
2	2.520	-	1.156
3	2.14	-	1.175
4	1.86	-	1.150
A	-	19190	
B	-	16580	1.155
C	-	14135	1.171
D	-	12170	1.160

CHLORINATION OF POLYSTYRENE IN SOLUTION.

a) Reaction Conditions.

250 mgs. samples of polystyrene were dissolved in 10 ml. A.R. carbon tetrachloride and the solutions were in turn transferred to reaction vessels attached to the vacuum system (Figure 7), using a hypodermic syringe. The amount of liquid in each reaction vessel was made up to 15 ± 0.5 mls. by adding washings from the flask and syringe. The reaction vessels were sealed at H, the solutions very thoroughly degassed and radiochlorine transferred in known amount as previously described. After the reaction vessels had been sealed off at G and thawed to room temperature they were immersed in a bath at 25 ± 1°, with exclusion of light, for one hour. The vessels were then opened and the polymer isolated as described subsequently.

b) Effect of Oxygen on the reaction.

In view of the known tendency of chlorine to react by free radical process in the presence of oxygen, the exclusion of air in the reaction was considered essential. Despite the fact that reaction was carried out in sealed tubes in the absence of air considerable difficulty was encountered in the earlier stages of this work due to irreproducibility of the amount of chlorine taken up by a polymer under fixed conditions. The cause of this was eventually traced to the presence of extremely small amounts of air. Chlorine uptake at 10^{-3} mm. pressure is considerably greater than at 10^{-1} or 10^{-5} mm. This was established by the following experiment.

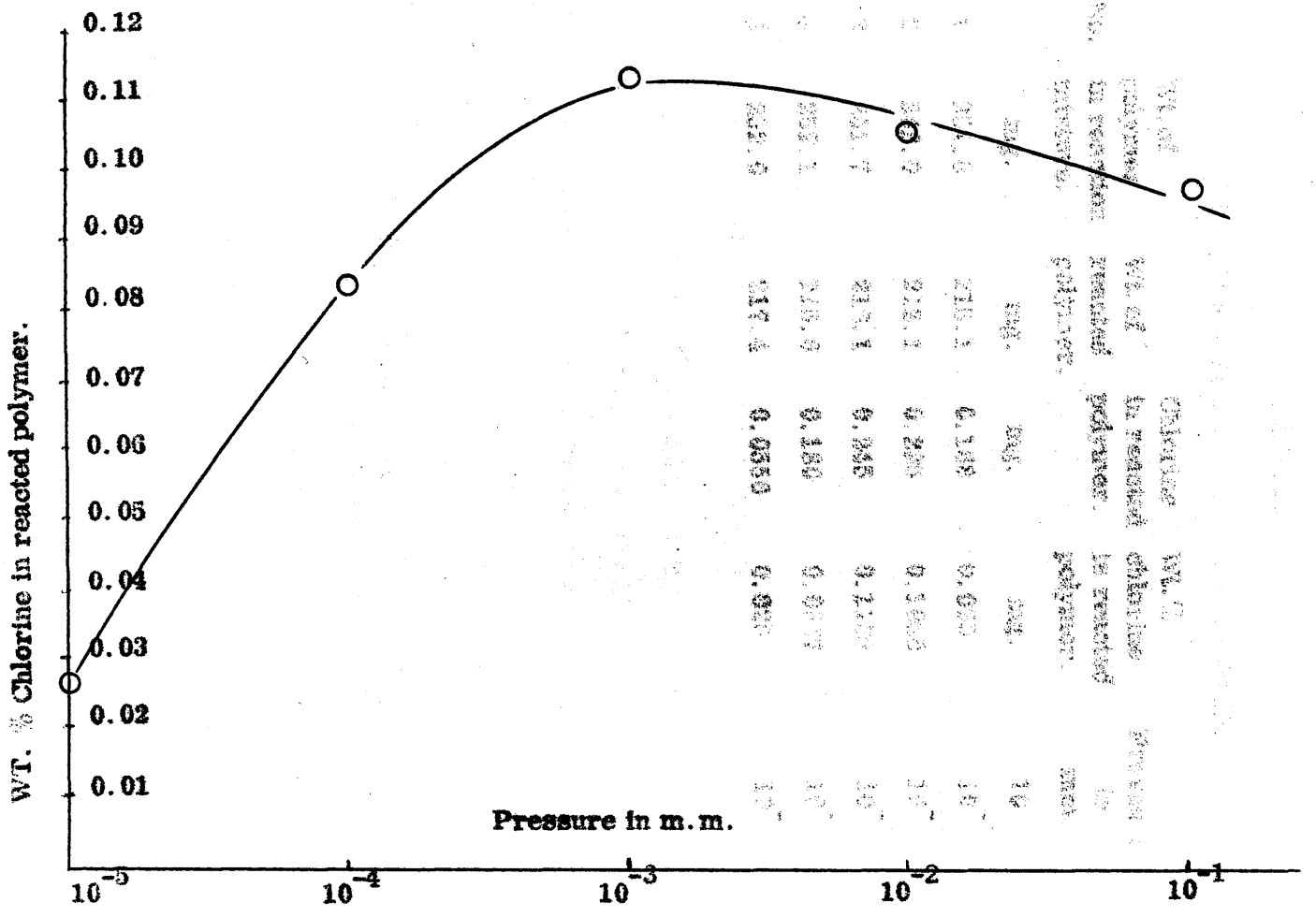


Figure 8 - Chlorine - Pressure relationship.

TABLE 5.

CHLORINE - PRESSURE RELATIONSHIP.

No.	Wt. of polymer in reaction mixture.	Wt. of reacted polymer.	Chlorine in reacted polymer.	Wt. % chlorine in reacted polymer.	Pressure in mm.
	mg.	mg.	mg.	mg.	10
1	251.8	215.1	0.188	0.083	10^{-1}
2	252.0	212.1	0.225	0.1050	10^{-2}
3	251.7	216.1	0.245	0.1135	10^{-3}
4	252.1	215.6	0.180	0.0837	10^{-4}
5	252.0	217.4	0.0556	0.026	10^{-5}

Five reaction mixtures were prepared, each containing 250 mgs of polymer and 2.5 mgs. of chlorine. Each mixture was very exhaustively degassed to an air pressure in the vacuum system of 10^{-5} mm. In the case of four of the tubes, small amounts of air were then admitted to give pressures of 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} mm; respectively. The tubes were sealed, and reaction and subsequent treatment of the polymers were as described in the appropriate sections of this thesis. When the activity of the polymer samples (expressed as wt. % Cl. present) was plotted against the air pressure during reaction, the result shown in Figure 8, was obtained, with a pronounced maximum at 10^{-3} mm. The data from which Figure 8, was obtained are given in Table 5.

In view of this very great care was taken in degassing reaction solutions to ensure that traces of air were not present. When this was done, reproducibility of the results was considerably improved.

PURIFICATION OF REACTED POLYMERS.

The first method tried was to shake the polymer solution with 10 mls of a decinormal solution of sodium thiosulphate in a separating funnel. After a few hours the carbon tetrachloride layer was separated off and the thiosulphate layer was washed with two lots of carbon tetrachloride which were added to the main solution. This solution was placed in the separating funnel and shaken up with 10 mls of decinormal sodium thiosulphate. The carbon tetrachloride layer was removed and made up to 20 mls, 10 mls of which were pipetted into a liquid counter and counted over one hour. The counts were corrected for dead time and background and knowing the specific activity of the radiochlorine the amount of chlorine combining with one grain of the polymer sample was calculated. This calculated quantity of chlorine was much higher than expected.

The solution of polymer in carbon tetrachloride after extraction with sodium thiosulphate was precipitated with methanol. The polymer was weighed after drying, dissolved in 12 mls of A.R. carbon tetrachloride and 10 mls were counted. The amount of chlorine combined with one grain of polymer was found to be less than that indicated by counting of the solution after extraction with sodium thiosulphate. It was concluded, therefore, that thiosulphate extraction does not remove completely all the unused chlorine and any radiochlorine-containing impurities in the reacted polymer solution.

The second method was to pour the polymer solution into 600 mls of methanol which was vigorously stirred using a magnetic stirrer. The polymer precipitated in a very finely divided state initially, however, when the rate of stirring was reduced the particle size gradually increased. The polymer was filtered immediately using a filter pad of No. 3 porosity. The polymer usually formed a dry skin or fine fibres which peeled easily off the filter pad. It was broken up into smaller pieces and placed in a vacuum desiccator which was evacuated using an oil pump. When dried it was weighed into a 12 mls. graduated flask, some A.R. carbon tetrachloride was added and when the polymer had dissolved the solution was made up to the graduation mark. 10 mls of the solution were pipetted into a liquid counter and counted. The polymer obtained after the first precipitation had a higher specific activity than the next one but the activity stayed constant after more than three precipitations.

All the reacted polymer samples were precipitated with methanol since this method appeared to give quite reliable and reproducible results.

COUNTING TECHNIQUE.

10 mls. portions of solutions were counted using a halogen quenched liquid counter (Mullard type MX 124/01, a Bendix Ericsson type 121 A scaling unit and a Bendix Ericsson 110 A probe unit). The paralysis time on the external quenching unit was set at 400μ seconds. The counter was supported in a Panax lead castle. The counter efficiency was checked periodically with a standard source, (uranyl nitrate solution) and was found to remain constant.

The plateau of the liquid counter was obtained by plotting applied voltage against counting rate while using the standard source. It had a plateau which extended over 100 volts and all counts were taken using an applied potential of 400 volts which lay one third of the way along the plateau. (Figure 9 and Table 6).

In each determination of polymer activity 10 mls of polymer/carbon tetrachloride solution were counted. Due correction was made for paralysis time and background and the activity of the polymer was expressed as counts per minute (c.p.m.) per gram of polymer. Knowing the specific activity of the radiochlorine used, the weight % chlorine in the polymer was readily calculated. When the counter was emptied of polymer solution, it was rinsed twice with carbon tetrachloride, twice with "pyroneg" solution and then twice with A.R. acetone. "RBX. 26" was also found to be a good cleaner for the counter. The counter was dried by blowing a jet of compressed air into it. At the end of each day the counter was

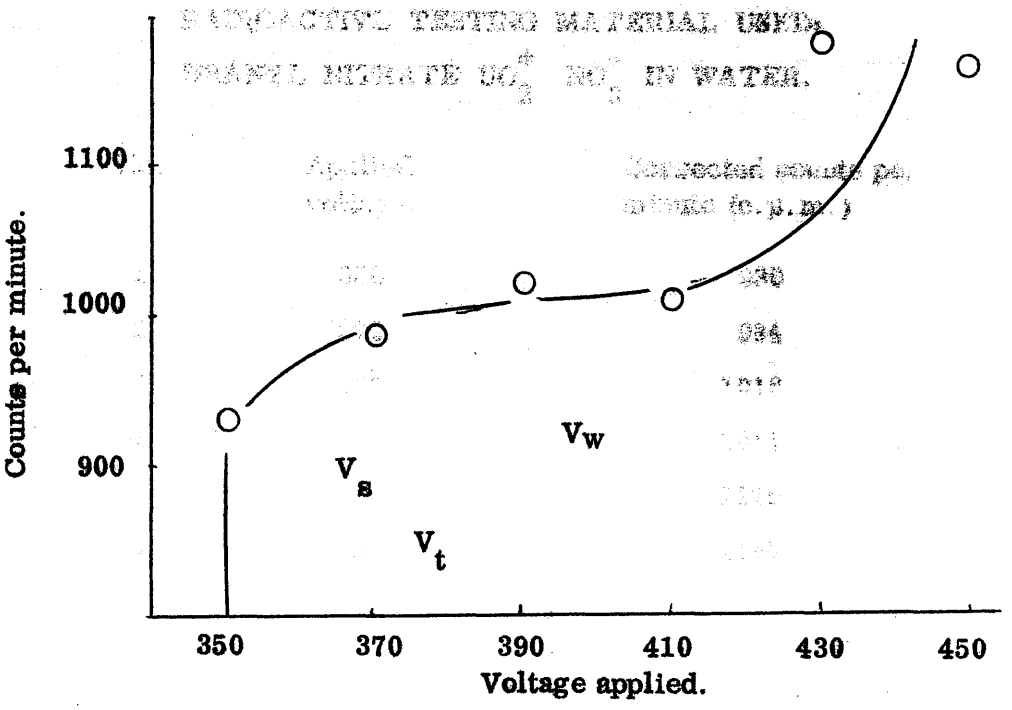


Figure 9 - Plateau for the geiger counter type Mx 124/01.

Vs = Starting potential.
Vt = Threshold potential.
Vw = Working potential.

TABLE 6.

PLATEAU OF LIQUID GEIGER COUNTER

TYPE MX. 124/01.

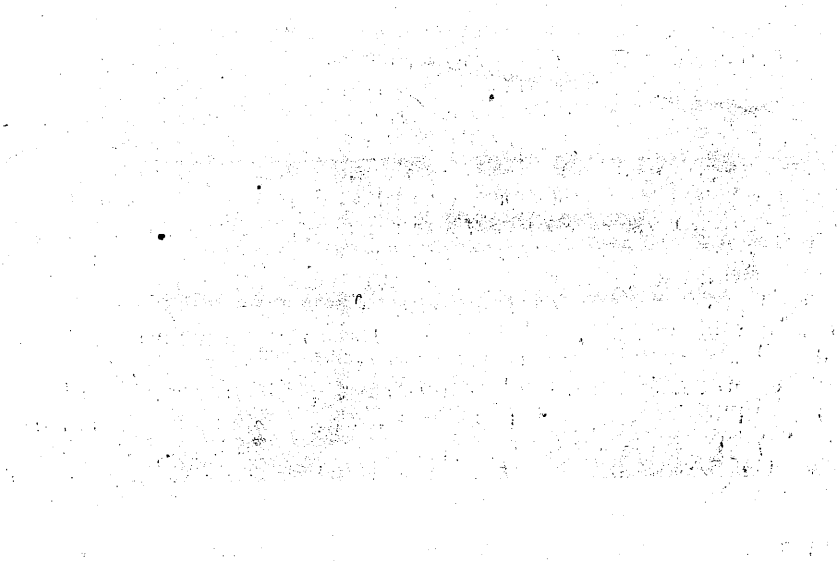
RADIOACTIVE TESTING MATERIAL USED:

URANYL NITRATE UO_2^+ NO_3^- IN WATER.

No.	Applied voltage.	Corrected counts per minute (c.p.m.)
1	350	930
2	370	984
3	390	1018
4	410	1011
5	430	1178
6	450	1163

filled with "REX. 25" solution and left overnight. The background counting rate was taken before counting every radiochlorinated polymer sample and was always between 10 - 15 c.p.m. When radiochlorine was absorbed in styrene and the solution counted, the counter was cleaned very carefully after use because activity seemed to be more easily absorbed by the glass of the counter.

Since the liquids counted were volatile the counter used had a ground glass stopper to check volatilization.



DEGRADATION EXPERIMENT.

A polystyrene fraction with number average molecular weight 425,000 was degraded at 325° in a glass tube under high vacuum. Three samples, each of approximately 200 mg ; were degraded to different extents. The residue in each case was dissolved in toluene and the number average molecular weight was determined using the MECHROLAB OSMOMETER. The relevant data are given in Table 7 and plotted in Figure 10.

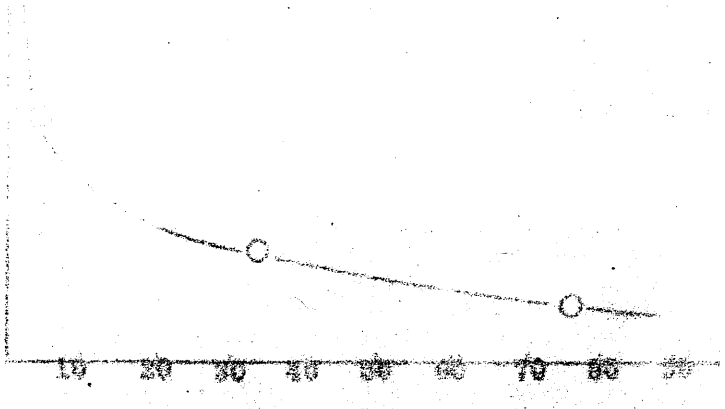


Figure 10 - Degradation experiment at 325° C.

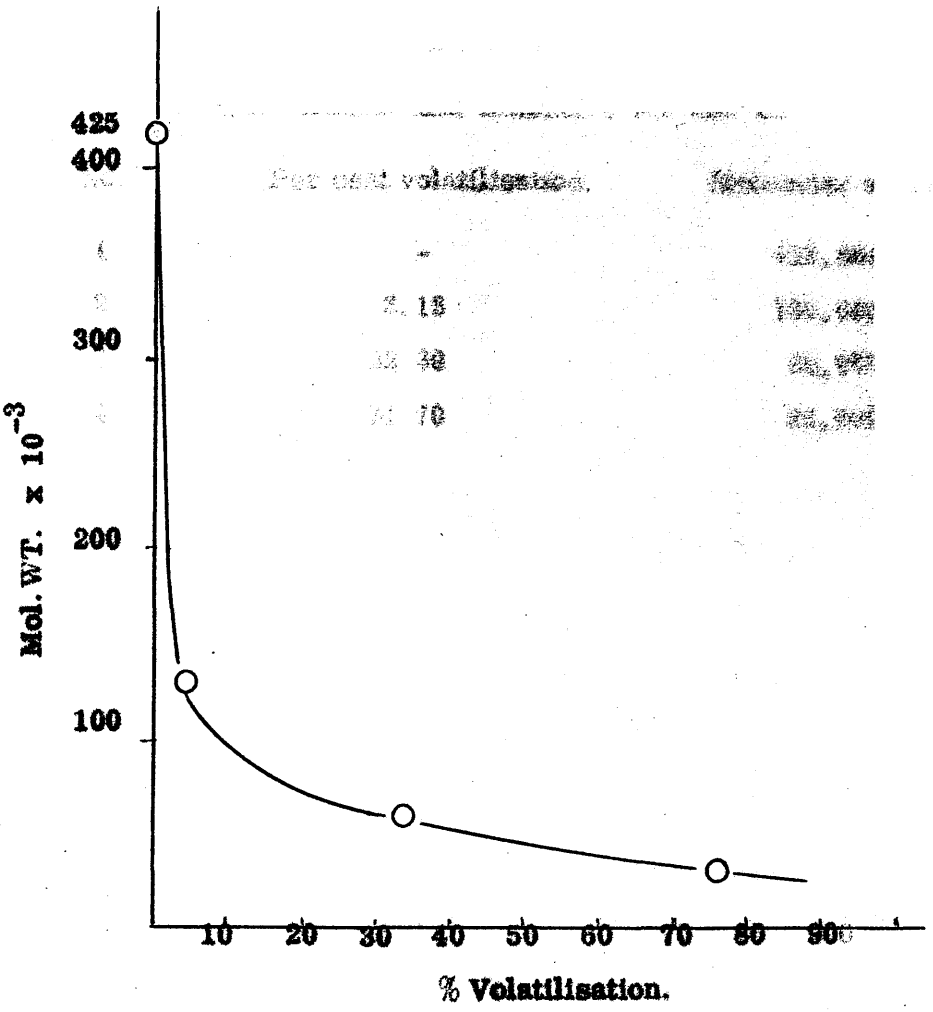
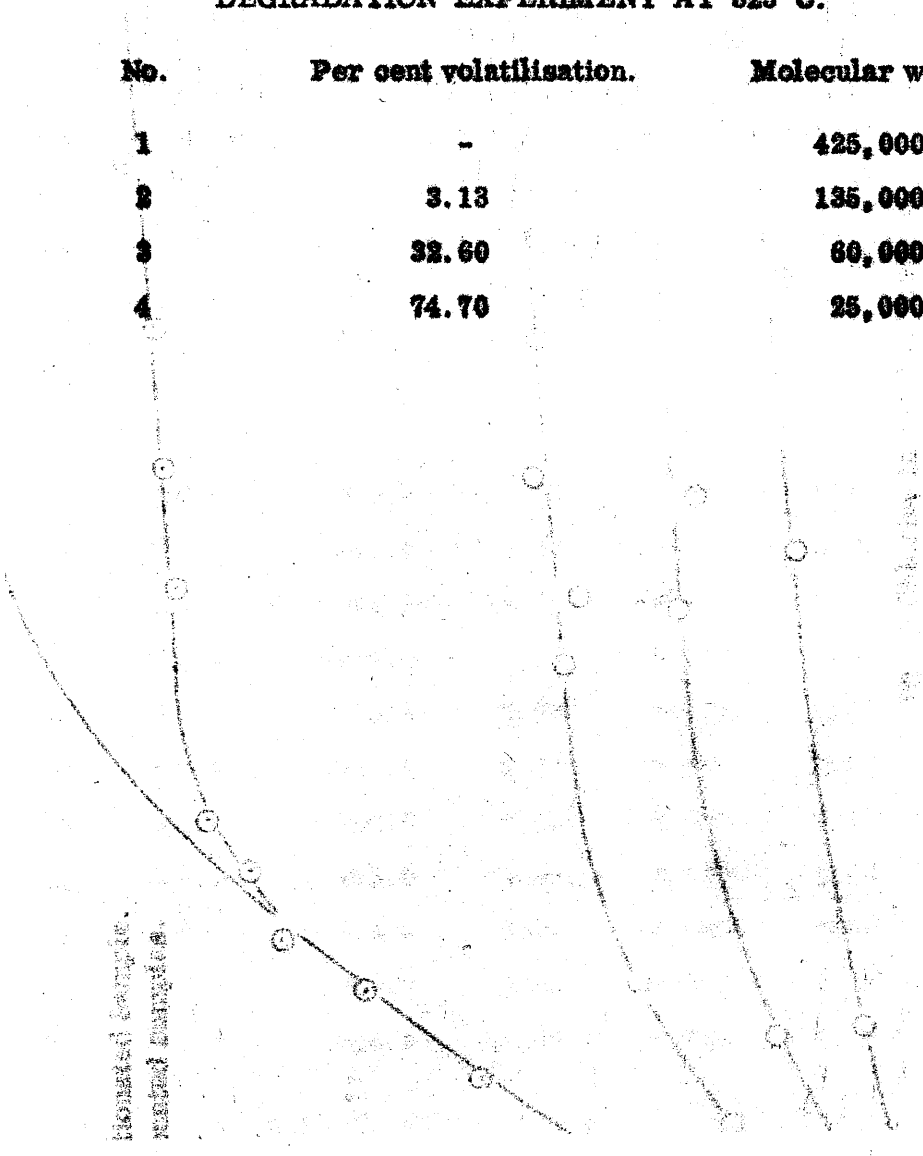


Figure 10 - Degradation experiment at 325°C.

TABLE 7.

DEGRADATION EXPERIMENT AT 325°C.

No.	Per cent volatilisation.	Molecular weight.
1	-	425,000
2	3.13	135,000
3	32.60	60,000
4	74.70	25,000



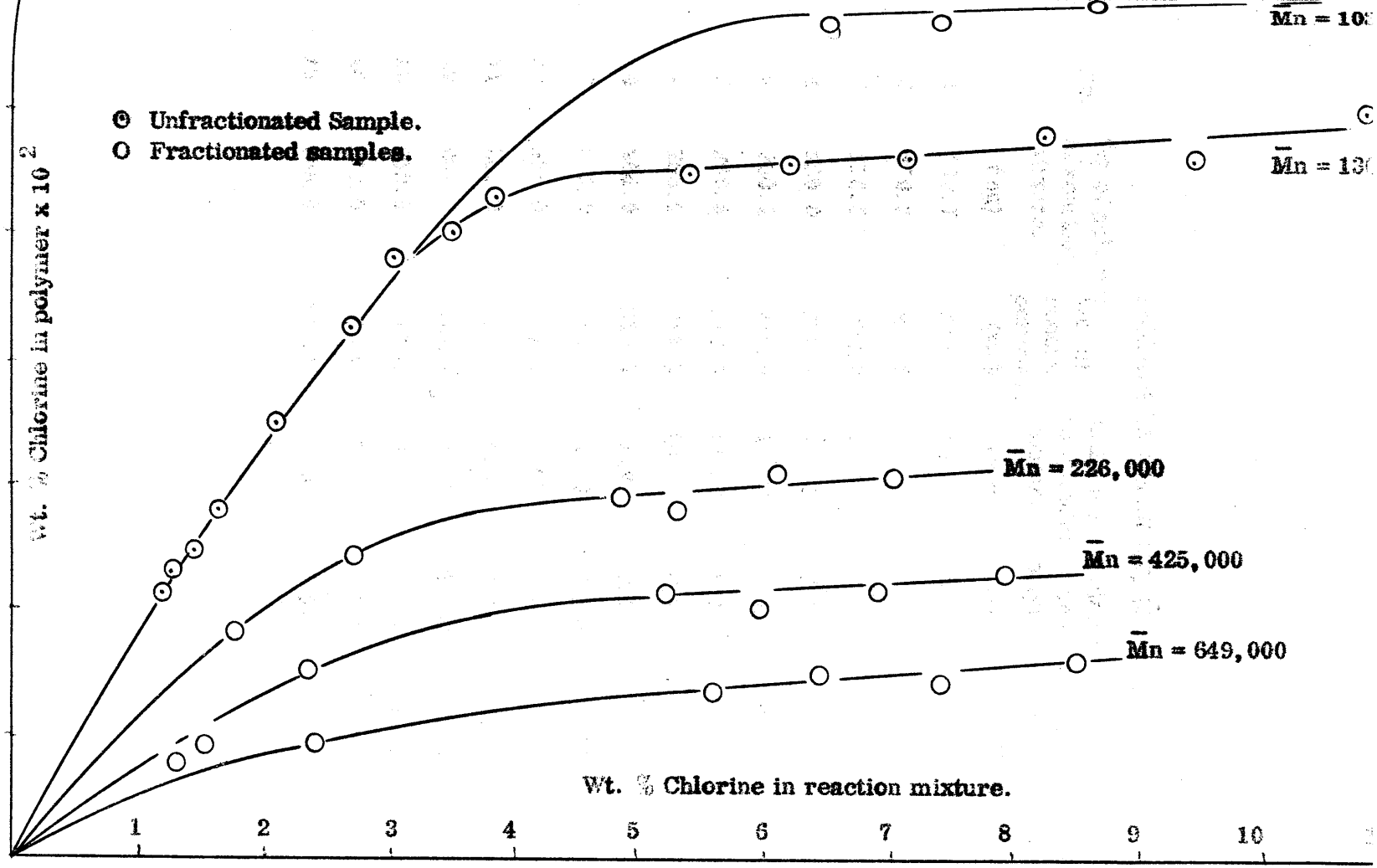


Figure 11 - Chlorination of polymer samples.

TABLE 8.

CHLORINATION OF UNFRACTIONATED POLYMERS

MOLECULAR WEIGHT, $\bar{M}n$ 130,000.

No.	Wt. of polymer in reaction mixture. (mg)	Wt. of reacted polymer. (mg)	Chlorine in reaction mixture. (mg)	Chlorine in reacted polymers. (mg)	Wt. % Chlorine in reaction mixture.	Wt. % Chlorine in reacted polymers.
1	250.7	202.1	30.35	0.121	10.81	0.0599
2	250.3	215.0	26.10	0.120	9.45	0.0558
3	250.0	208.0	22.45	0.121	8.24	0.0581
4	250.0	213.1	19.30	0.119	7.17	0.0560
5	250.4	212.9	16.60	0.118	6.22	0.0557
6	250.4	217.4	14.28	0.120	5.39	0.0552
7	255.0	211.5	10.21	0.112	3.85	0.0530
8	254.0	216.3	9.02	0.108	3.52	0.0500
9	253.0	215.5	7.99	0.104	3.05	0.0483
10	255.0	214.1	7.07	0.091	2.70	0.0425
11	251.0	206.8	4.91	0.073	2.12	0.0353
12	252.0	215.0	4.34	0.060	1.66	0.0279
13	252.0	215.0	3.84	0.053	1.47	0.0246
14	253.0	206.2	3.39	0.047	1.33	0.0228
15	256.0	216.1	3.00	0.045	1.18	0.0208

TABLE 9.

CHLORINATION OF FRACTIONATED POLYMERS.

No.	Wt. of polymer in reaction mixture. (mg)	Wt. of reacted polymer. (mg)	Chlorine in reaction mixture. (mg)	Chlorine in reacted polymers. (mg)	Wt. % Chlorine in reaction mixture.	Wt. % Chlorine in reacted polymers.
		$\bar{M}n = 649,000$ - Sample 4.				
1	252.2	23.45	229.7	0.0367	8.50	0.016
2	251.6	20.15	230.7	0.0323	7.42	0.014
3	251.3	17.30	232.1	0.0348	6.46	0.015
4	251.1	14.88	231.7	0.0312	5.60	0.0135
5	252.5	6.25	232.0	0.0209	2.42	0.009
6	251.8	3.27	230.9	0.0173	1.30	0.075
		$\bar{M}n = 425,000$ - Sample 3.				
1	250.4	210.0	21.50	0.0488	7.90	0.0232
2	251.8	203.1	18.48	0.0436	6.88	0.0215
3	250.5	208.2	15.88	0.0415	5.97	0.020
4	250.3	203.5	13.63	0.0436	5.19	0.0215
5	250.6	216.0	5.97	0.0324	2.33	0.015
6	250.8	208.8	3.80	0.0187	1.50	0.009

TABLE 10.

CHLORINATION OF FRACTIONATED POLYMERS.

No.	Wt. of polymer in reaction mixture. (mg)	Wt. of reacted polymer. (mg)	Chlorine in reaction mixture. (mg)	Chlorine in reacted polymers. (mg)	Wt. % Chlorine in reaction mixture.	Wt. % Chlorine in reacted polymers.
		$\bar{M}n$ = 226,000 - Sample 2.				
1	250.0	207.6	18.88	0.0632	7.06	0.0305
2	250.2	219.0	16.23	0.068	6.10	0.0310
3	250.2	207.3	14.00	0.058	5.30	0.028
4	250.3	209.8	12.20	0.0607	4.83	0.029
5	250.4	209.0	6.94	0.0502	2.70	0.024
6	250.0	220.1	4.48	0.0396	1.74	0.018
		$\bar{M}n$ = 103,000 - Sample 1.				
1	250.0	211.4	27.50	0.149	9.93	0.071
2	250.0	210.4	23.63	0.148	8.65	0.069
3	250.0	206.8	20.03	0.138	7.43	0.067
4	250.0	209.0	17.50	0.140	6.50	0.067

PART III

RESULTS AND DISCUSSION.

CALCULATION OF UNSATURATIONS FROM CHLORINATION DATA.

(i) Calculation of weight per cent chlorine in reacted samples.

The plots of weight per cent chlorine in polymer versus weight per cent chlorine in the reaction mixture indicate that once double bonds have reacted, further reaction of the polymer with chlorine, under the conditions of the experiments, is very small. This is shown by the small gradient of the linear portion of the graphs. A small correction may be made for this side reaction, and a value corresponding to complete reaction of double bonds present with chlorine may be obtained, by extrapolating the linear portion to the axis.

When this was done the results of the Table 8 were obtained, where the unsaturation is expressed on a weight per cent basis as weight per cent chlorine in the polymer.

(ii) Assumptions involved in calculating unsaturations.

The results just referred to give a measure of polymer unsaturation but they do not indicate directly the number of double bonds per chain or the molar unsaturation. In order to obtain these quantities it is necessary to make an assumption regarding the nature of the reaction of polystyrene with chlorine. Chlorine reacts with double bonds in different environments in different ways: some substances (e.g. styrene monomer) give direct addition of chlorine,

others (e.g. isobutene monomer) give substitution.[51,52]

McNeill[37] was able to show that in the reaction of chlorine with butyl rubber two chlorine atoms react per original double bond, but the reaction involved is one of substitution. When the polymer unsaturation is as low as in the present work, however, direct determination of the nature of the reaction becomes impossible and it is necessary to rely on an assumption of the nature of the reaction based on comparison of the unsaturated polymer structure with that of simpler molecules of related structure whose behaviour with chlorine has been studied. The nature of the reaction of the monomer with chlorine may be known, and if not, this can easily be established, so that the simplest approach is to assume that the reaction follows a similar course in the case of double bonds in the polymer.

In the case of polystyrene, the polymer is assumed to add two chlorine atoms per original double bond.

(iii) Specimen calculation.

If the weight per cent chlorine (extrapolated) in the polymer, W, and the number average molecular weight, $\bar{M}n$, are known, then the number of double bonds per polymer chain, c, may be calculated as follows:

c = no. of double bonds per chain

= no. of moles of double bonds per mole of polymer

= no. of moles of chlorine in polymer per mole of polymer.

$$= \frac{\text{g. of Cl2}}{70.9} \times \frac{\bar{M}n}{\text{g. of polymer}} = \frac{\text{g. of Cl. 2}}{\text{g. of polymer}} \times \frac{\bar{M}n}{70.9}$$

$$= {}^{W}/_{100} \times {}^{\bar{M}n}/_{70.9} = \frac{W\bar{M}n}{7.09} \times 10^{-3}$$

$$= 1.41\ W\bar{M}n \times 10^{-4}$$

Thus in the case of sample 1 in Table 10 we have

$W = 0.0625\%$ $\bar{M}n = 103,000$

$$c = 1.41 \times 0.0625 \times 10.3 \times 10^{4} \times 10^{-4}$$

$$= 0.91$$

i.e. slightly less than one double bond per polymer chain.

The unsaturation of the remaining samples can be calculated in the same way, giving the results of the last column of Table 11.

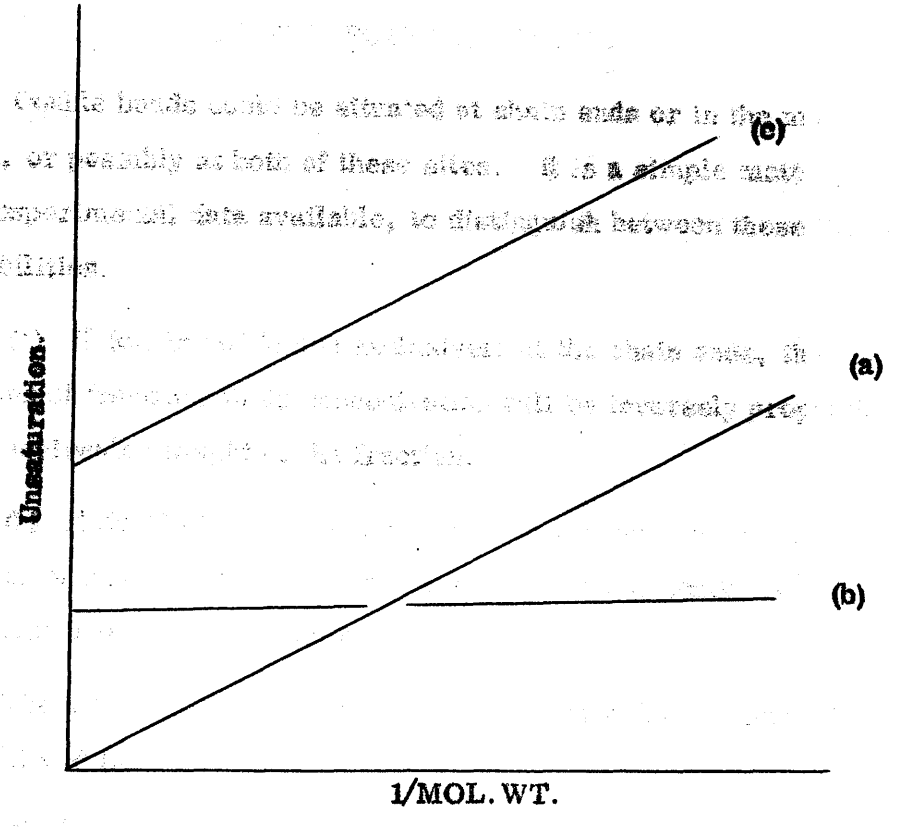


Figure 13 – Effect of location of double bonds in polymer on the relation between unsaturation and 1/mol. wt.
(a) double bonds only at ends.
(b) double bonds only in main chain.
(c) both types of double bonds present.

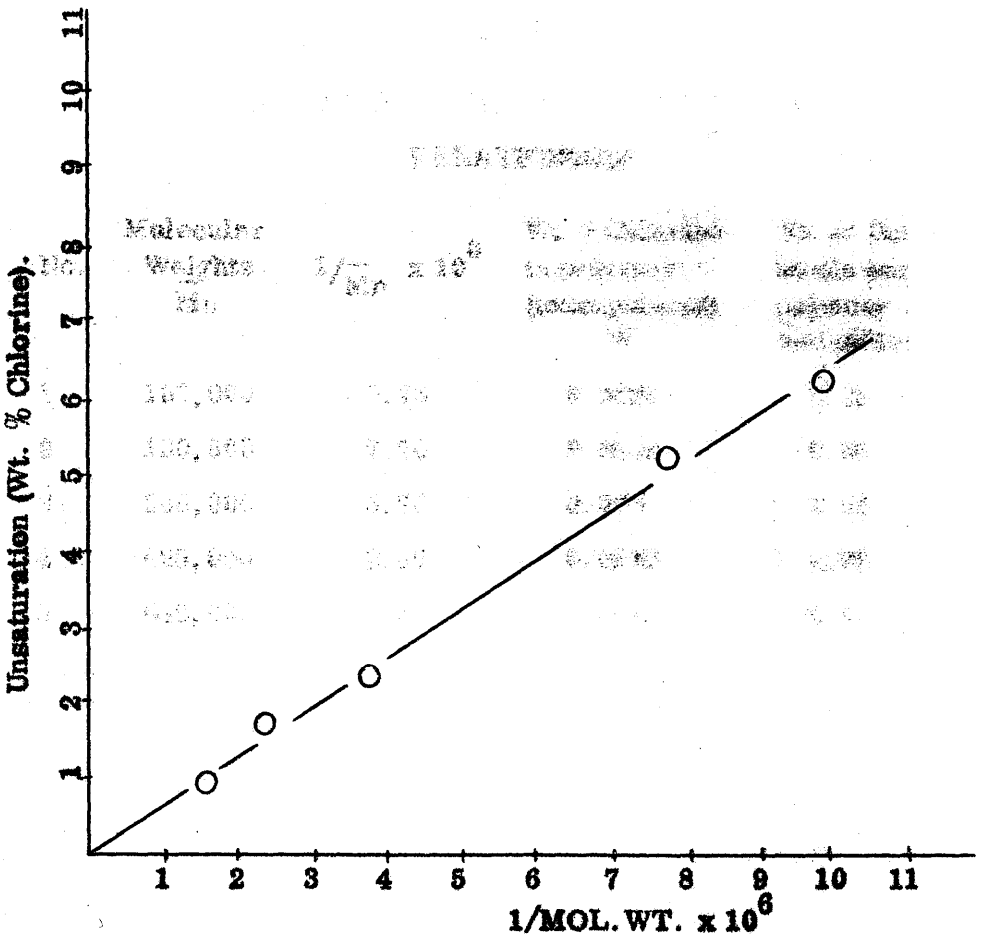


Figure 12 - Molecular weight - unsaturation relationship.

LOCATION OF THE DOUBLE BONDS IN THE POLYMER CHAIN.

Double bonds could be situated at chain ends or in the main chain, or possibly at both of these sites. It is a simple matter, with experimental data available, to distinguish between these three possibilities.

(a) If double bonds are exclusively at the chain ends, then in a series of fractions their concentration will be inversely proportional to the molecular weight of the fraction.

(b) If double bonds are exclusively in the main chain, then in a series of fractions their concentration will be independent of the molecular weight of the fraction.

These two situations are illustrated graphically in Figure 13, lines (a) and (b).

(c) When both types of double bonds are present the line (c) in Figure 13 would be obtained, making an intercept on the unsaturation axis corresponding to the main chain unsaturation. Thus both types can be distinguised and estimated.

The present results for polystyrene are shown in Figure 12, where W is plotted against $^{1}/_{\overline{M}n} \times 10^{6}$ for a series of fractions. It is clear that, since the line passes through the origin, double bonds must be situated <u>exclusively</u> at the chain ends.

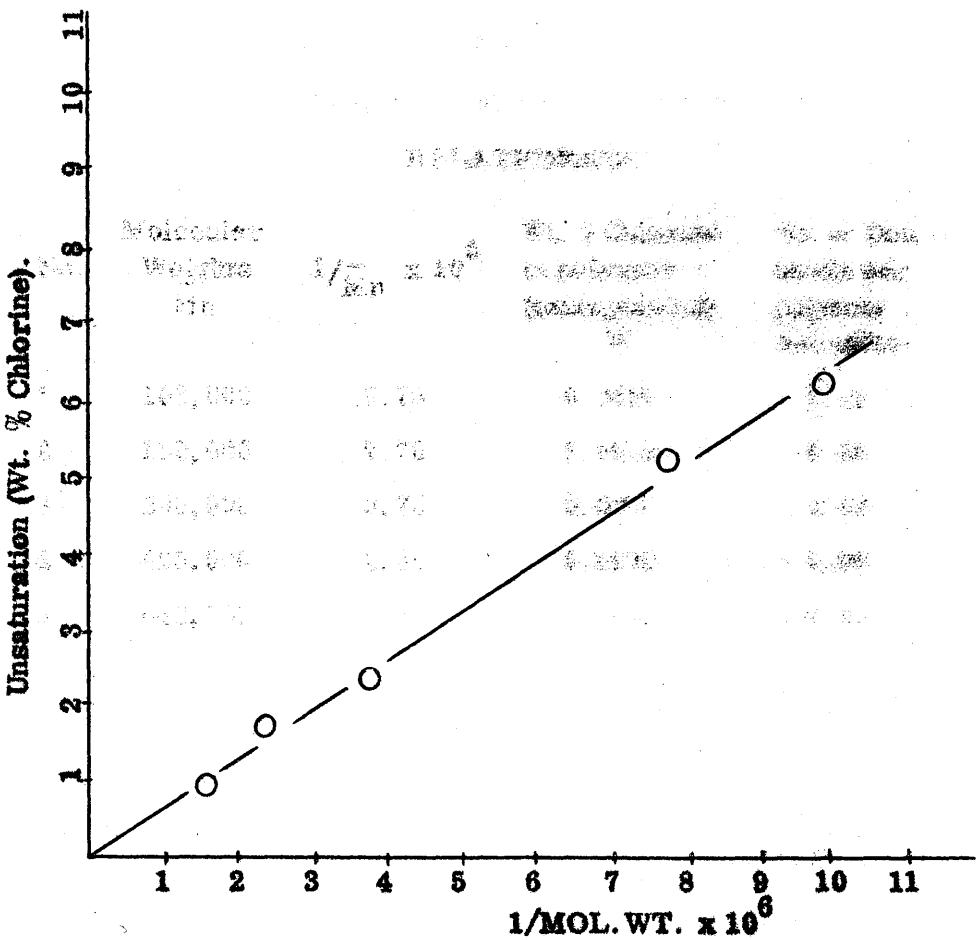


Figure 12 - Molecular weight - unsaturation relationship.

TABLE 11.

MOLECULAR WEIGHT - UNSATURATION RELATIONSHIP.

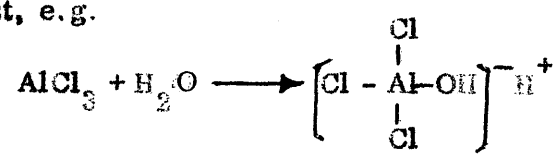
No.	Molecular Weights M_n	$1/\overline{M}_n \times 10^6$	Wt. % Chlorine in polymer (extrapolated) W	No. of Double bonds per polymer molecule.
1	103,000	9.75	0.0625	0.91
2	130,000	7.70	0.0520	0.95
3	266,000	3.76	0.0235	0.88
4	425,000	2.35	0.0170	1.02
5	649,000	1.54	0.0095	0.96

RELEVANCE TO: a) 'CATIONIC' TERMINATION.

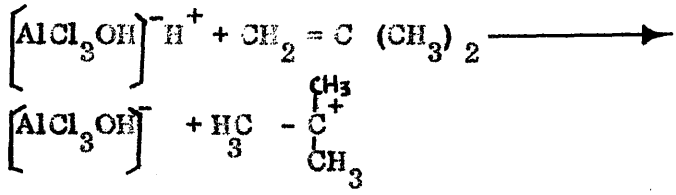
b) WEAK LINK THEORY.

a) Relevance to 'Cationic' termination.

For a polymerisation to proceed cationically, it must first be initiated by a Lewis acid. In many cases, the actual initiating acid is the product of a reaction between a catalyst and cocatalyst, e.g.



In this instance, the Lewis acid, aluminium chloride, reacts with a trace of moisture to give a proton plus a complex negative ion. The proton then initiates the polymerisation. The negative ion, which had been associated with the proton, then becomes associated with the positive carbonium ion which is at the propogating end of the chain. The initiation of isobutylene polymerisation is given below:



Polymerisation proceeds by addition of the carbonium ion chain end to the double bond of a monomer.

Identification of cationic termination in the chemical sense is only at a rudimentary stage, and for most processes rest on

plausibility rather than any direct demonstration. Termination processes can be subdivided into two groups.

A) Chain termination mechanisms resulting in unsaturation.

i) By mutual neutralisation of cationic chain and anionic fragment of catalyst.

ii) By isomerisation or fission to non-propagating cation.

B) Other mechanisms of chain termination.

i) By proton transfer to monomer.

ii) By proton transfer to solvent if solvent an acceptor; by anionic capture if solvent is an anion donor; by substitution in an aromatic solvent.

iii) Transfer to chain breaking agents or impurities by mechanisms (ii).

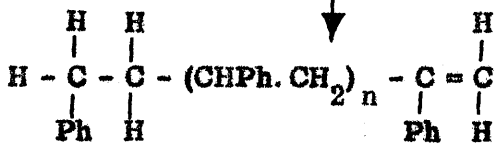
Based on theoretical expectations, these are accepted mechanisms which are discussed in detail in Part I.

In principle, any process that leaves a terminal double bond in the polymer e.g. from a proton transfer to catalyst, co-catalyst or solvent, should be fairly easy to detect by using this radiochemical technique.

The following possible termination mechanisms have been very recently suggested for the styrene - $SnCl_4$ system by Reilly, Pepper[38] and supported by Plesch and Gandini[39], who regard the system as 'pseudocationic'.

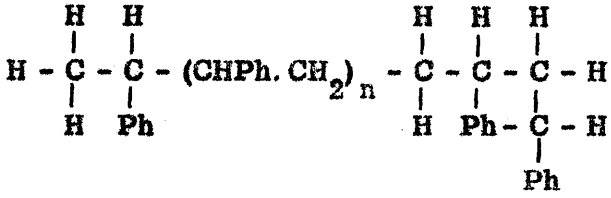
Termination

$$\left[HO.SnCl_4 . (CHPh.CH_2)_3 . (CHPh.CH_2)_n . CHPh.CH_3\right] \text{ Solv.}$$



Unsaturated group.

OR



Indene type saturated group.

Qualitative evidence of characteristic end groups has occasionally been deduced from the infra-red spectra of the polymers e.g. t - butyl and unsaturated end groups in polyisobutene [40] and chlorine in polystyrene polymerised in ethylene dichloride by $TiCl_4$ [41]. Such evidence is usually not very well confirmed. The first steps towards quantitative identification have been made in these investigations.

The results of chlorination indicated that there was one double bond per polymer chain in polystyrene prepared as described and a plot of unsaturation against the inverse of the number average molecular weight gave a straight line passing through the origin indicating that the unsaturation was exclusively terminal. This supports the proton expulsion theory of chain termination in the

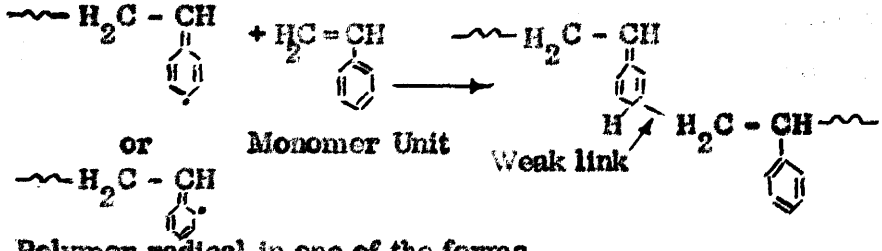
above mentioned 'cationic' and 'pseudocationic' systems and clearly shows that under the conditions of polymerisation employed for these polymers other chain termination processes are of negligible importance.

b) Relevance to weak link theory.

On one hand Jellinek[42], and Grassie and Kerr[43] maintain that the initial sharp decrease in molecular weight during degradation of polystyrene is due to the scission of a limited number of weak links to form stable molecules. On the other hand, Sinha and Wall[44], proposed that it was due to intermolecular transfer in which polymer radicals abstracted tertiary hydrogen atoms from polystyrene chains, chain scission subsequently occurring at these points.

i) Degradation experiments (Figure 10) indicate similar behaviour in polystyrene prepared by a 'cationic' mechanism to that observed by earlier workers for polystyrene by free radical mechanism. Therefore, if the initial drop is due to weak links, these are also present, and in similar concentration to the supposed weak link in free radical polystyrene.

ii) Grassie and Kerr[45], Grassie and Cameron[46] came to the conclusion that the polymer contains weak links and that these are associated with unsaturated structures in the main chain, arising by a mechanism proposed to be:



Polymer radical in one of the forms.

This theory obtained some support from ozonolysis experiments carried out by Grassie and Cameron[47] which appeared to indicate a close correlation between the unsaturation measured and the weak link concentration calculated from the molecular weight drop or degradation.

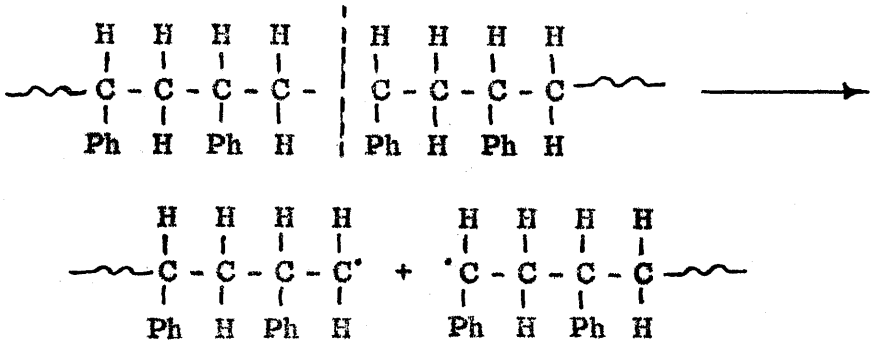
On the basis of this theory, polystyrene samples showing a sharp initial molecular weight drop on degradation must contain main chain unsaturation.

The chlorination data of the present work indicate very clearly that polystyrene prepared by cationic mechanism contains no main chain double bonds whatever, yet it degrades in the same way as other polystyrene samples.[49]

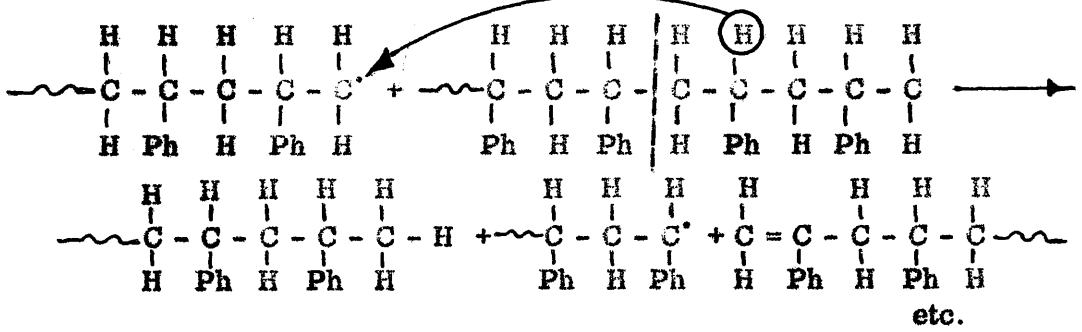
It may be deduced, therefore, that if there are weak links present, these are not associated with double bonds, as was proposed by these authors.

The remarkable similarity in degradation behaviour of polystyrene prepared by such fundamentally different mechanisms suggests that an explanation must be looked for along the lines proposed by Madorsky and his co-workers[50], who suppose that weak links, if they exist, contribute only partially to molecular weight drop, and that random scissions must be assumed to occur:

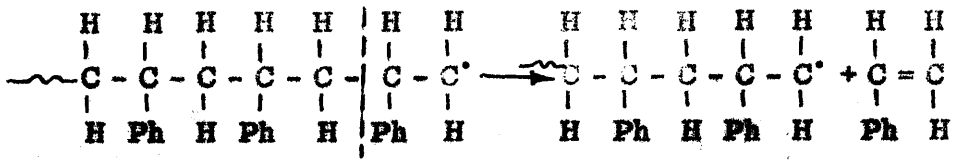
I) **Scission without hydrogen transfer.**



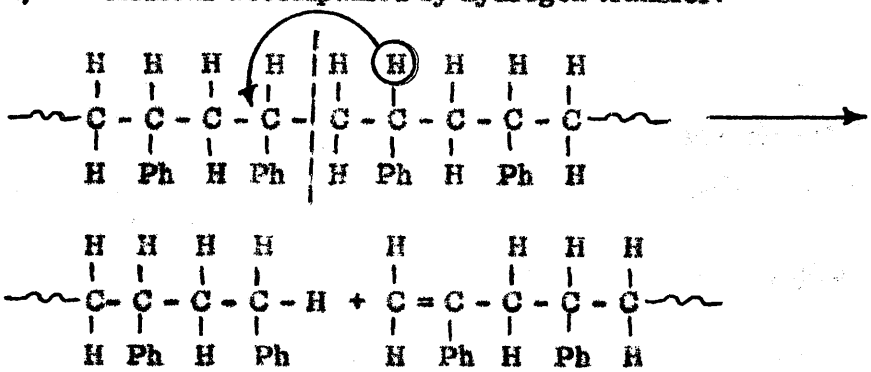
Each one of the two free radicals may then remove a hydrogen inter or intramolecularly to cause new scissions (free radical transfer).



Free radicals will unzip to yield monomer.



II) Scissions accompanied by hydrogen transfer.



The apparent stabilisation after the initial sharp drop is explained by assuming that the drop due to random scissions is then counter-balanced by disappearance of smaller chains through unzipping, mainly to monomer.

REFERENCES

1. Grassie, N. and Melville, H. W., Proc. Roy. Soc., 199, A, 1, (1949).
2. Grassie, N. and Vance, E., Trans. Faraday Soc. 49, 184, (1953).
3. Plesch, P. H., Chemistry of Cationic Polymerisation, Pergamon, London (1963).
4. Plesch, P. H., Progress in High Polymers, Vol. 2., ed. J. C. Robb and F. W. Peaker, Heywood, London (1963).
5. Pepper, D. C., Progress in High Polymers, Vol2., ed. J. C. Robb and F. W. Peaker, Heywood, London (1963).
6. Plesch, P. H. and Gandini, A., Proc. Chem. Soc. London, 113, (1964).
7. Kennedy, J. P. and Langer, A. W., Advances Polymer Sci., 3, 508, (1964).
8. Evans, A. G., James, E. A. and Owen, E. D., J. Chem. Soc., 3532 (1961).
9. Evans, A. G., Jones, N., Jones, P. M. S. and Thomas, J. H., J. Chem. Soc., 2757, (1956). J. Chem. Soc., 104, (1957).
10. Jellinek, H. H. G., J. Polymer. Sci., 3, 850, (1948).
11. Madorsky, S. L. and Straus, S., J. Research Nat'l Bur. Standards 40, 417, (1948). 50, 165, (1953).
12. Grassie, N. and Kerr, W. W., Trans. Faraday Soc., 53, 234, (1956).
13. Grassie, N. and Cameron, G. G., Polymer, 2, 367, (1961).
14. Madorsky, S. L., J. Polymer. Sci., 9, 133, (1952).
15. Jellinek, H. H. G., Degradation of vinyl polymers, Academic Press, New York (1955).
16. Simha, R., Wall, L. A. and Blatz, P. J., J. Polymer. Sci., 5, 615, (1950).
17. Simha, R. and Wall, L. A., J. Phys. Chem., 56, 707, (1952).

18. Simha, R., Trans. N. Y. Acad. Sci., 14, 151, (1952).

19. Simha, R., Nat. Bur. Stand. Circ., 39, 525, (1953).

20. Gordon, M. Trans. Faraday Soc., 53, 1662, (1957).

21. Gordon, M. and Shenton, L. R., J. Polymer Sci., 88, 157 and 179 (1959).

22. Gallo, S. G., Weise, H. K. and Nelson, J. F., Ind. Eng. Chem. (Industr.) 40, 1277, (1948).

23. Lee, T. S., Kolthoff, I. M. and Johnson, E., Analyt. Chem., 22, 995, (1950).

24. McNall, L. R. and Eby, L. T., Analyt. Chem., 29, 951, (1957).

25. Kaufmann, H. P., Studien auf dem Fettgebiet, Verbag Chemie, Berlin, (1935).

26. Byrne, R. E. and Johnson, J. B., Analyt. Chem., 28, 126, (1956).

27. McNeill, I. C., Polymer, 4, 22, (1963).

28. McNeill, I. C., Polymer, 4, 15, (1963).

29. Makhdumi, T. M. and McNeill, I. C., Unpublished.

30. Mounter, D. and McNeill, I. C., Unpublished.

31. McGuchan, R. and McNeill, I. C., Unpublished.

32. McNeill, I. C., Polymer, 4, 247-257, (1963).

33. Steele, R. E., Walker, W. E., Burge, D. E. and Ehrmantrant, H. C., Conference on Analyt. Chem., Pittsburg, (1964).

34. Vaughan, M. F., Nature, 188, 55, (1960). Nature, 195, 801, (1962).

35. Flory, P. J., J. Amer. Chem. Soc., 65, 372, (1943).

36. Alfrey, T., Bortovics, A. and Mark, H., J. Amer. Chem. Soc., 65, 2319, (1943).

37. McNeill, I. C., J. Chem. Soc., 639, (1961).

38. Reilly, P.J. and Pepper, D.C., J. Polymer Sci., 58, 639, (1962).

39. Gandini, A. and Plesch, P.H., J. Polymer. Sci., 3, 127, (1965).

40. Plesch, P.H., Proceedings of the Symposium on Chemistry of Polymerisation Processes, S.C.I., London (1965).

41. Pepper, D.C., Quarterly Reviews of the Chemical Society, 8, (1954).

42. Jellinek, H.H.G., J. Polymer Sci., 4, 13, (1949).

43. Grassie, N. and Kerr, W.W., Trans. Faraday Soc., 55, 1050, (1959).

44. Simha, R. and Wall, L.A., J. Polymer Sci., 6, 39, (1951).

45. Grassie, N. and Kerr, W.W. Proceedings of International Symposium on Macromolecules, Wiesbaden, Sect. III B, No. 11. (1959).

46. Grassie, N., Cameron, G.G. and Thompson, S.J., J. Chem. Soc. 1411, (1960).

47. Grassie, N. and Cameron, G.G., Makromol. Chem. 51, 130-136, (1962).

48. Brockhaus, A. and Jenckel, E., Makromol. Chem., 18/19, 262, (1956).

49. Grassie, N., Chem. and Ind., 537-542, (1957).

50. Madorsky, S.L., Thermal Degradation of Organic Polymers, Interscience, New York, (1964).

51. Haider, S.I., Malhdumi, T.M. and McNeil, I.C., Unpublished.

52. Mayer, G., Kuriacose, J.C. and Eschard, F., Bull. Soc. Chem. Fr. 624 (1961).

A C K N O W L E D G E M E N T

I take this opportunity to acknowledge my great indebtedness to my friend Malik Mohammad Rafiq for his constant help and encouragement during the course of this research project.

S. I. H.